

**QUALITATIVE, QUANTITATIVE AND KINETIC STUDIES
OF SALTS AND POLYMERS WITH A NEW PYROLYZER
IN COMBINATION WITH A GAS CHROMATOGRAPH.**

by

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**Analytical Chemistry
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Inger Ericsson

fil.lic., Vrm1

To my mother,
husband and children

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A GAS CHROMATOGRAPH.

The thesis consists of a summary and the following papers.
In the summary these papers will be referred to by I-VII.

- I I. Tydén, Gas Chromatographic Study of the Pyrolysis of Potassium Salts of Xanthic Acids, *Talanta* 13, 1353 (1966).
- II I. Tydén-Ericsson, A New Pyrolyzer with Improved Control of Pyrolysis Conditions, *Chromatographia* 6, 353 (1973).
- III I. Ericsson, Temperature Calibration of a Platinum Foil for Pyrolysis Gas Chromatography. Submitted.
- IV I. Ericsson, Decomposition Studies of Cis-1.4-Polybutadiene by Pyrolysis Gas Chromatography. Part I: Pyrolysis at low temperatures with short temperature rise times. Submitted.
- V I. Ericsson, Decomposition Studies of Cis-1.4-Polybutadiene by Pyrolysis Gas Chromatography. Part II: Pyrolysis to different end-temperatures, temperature rise times, amounts and areas. In manuscript.
- VI L. Andersson and I. Ericsson, Studies of Pyrolysis Conditions for Qualitative, Quantitative and Kinetic Analyses of Polystyrene by Pyrolysis Gas Chromatography. In manuscript.
- VII I. Ericsson, Quantitative Pyrolysis Gas Chromatography. Simultaneous determination of two barbituric acids in a tablet formulation. In manuscript.

SUMMARY.

Introduction:

Since 1860, when C.G. Williams isolated isoprene from natural rubber, pyrolysis has been a useful tool for determining the nature and structure of polymers.

Pyrolysis was combined with mass spectrometric, infrared or ultraviolet techniques for the analysis of the decomposition products. In 1954 Davison et al. [1] suggested that pyrolysis be combined with the gas chromatographic techniques and today most pyrolyzers are linked to gas chromatographs. The combination of the pyrolyzer and the gas chromatograph is advantageous in two ways. The gas chromatograph analyses the products of pyrolysis both quantitatively and qualitatively and the field of gas chromatography has been extended because it is now possible to make analyses of compounds having high boiling components. Most of the work in pyrolysis gas chromatography (PGC) prior to 1970 has been reviewed previously [2,3].

In december 1968 there was an Inaugural Meeting of the Pyrolysis Sub Group of the Gas Chromatography Discussion Group. The aim of this Sub group was to rationalize and standardize pyrolysis gas chromatography. Replies to a questionnaire circulated to the members, suggested that the primary interest of pyrolysis gas chromatography (PGC) was in the identification of synthetic polymers, but it was recognised that if there were improvements in the precision of PGC, research interest in the use of PGC, for quantitative and structural studies will increase.

In the case of pyrolysis gas chromatography precision, the greatest advantage would come from an improvement in the determination and the reproducibility of the pyrolysis temperature. The temperature rise should be very rapid and when the predetermined temperature is achieved it should remain constant for a known time and decrease as rapidly as possible after pyrolysis is over. If conditions

of pyrolysis are known, standardization of the pyrograms for qualitative analysis becomes possible. Several attempts [4,5,6] have been made to standardize pyrograms but there are still many difficulties to overcome [6].

At the beginning of this work a very simple pyrolyzer was constructed [I]. The results of studies, in which salts of xanthic acids were pyrolyzed, and reports in the literature suggested that considerable improvement might be obtained if more attention were given to pyrolyzer design particularly in the ability of the user to control the pyrolysis conditions.

The work was carried out in three stages. The first was the construction of a new pyrolyzer which could be adapted to suit varying known pyrolysis conditions [II, III]. The second part was an investigation into the conditions required for kinetic, qualitative and quantitative determinations [IV, V, VI] and the third should show that it was possible to solve a practical quantitative problem with the new pyrolyzer [VII].

Apparatus:

The pyrolysis unit which was described in the first paper [I] consisted of a platinum foil pyrolyzer. When pyrolyzing a salt (of xanthic acid) the reproducibility of the heights of the chromatographic peaks could be regarded as being relatively good, but the temperature rise time (TRT) was too long. To shorten the TRT and to keep the temperature constant, independent of the temperature of the surroundings, the platinum foil was constructed as one arm of a Wheatstone bridge and a resistance was built into the bridge using a relay (fig). When pyrolyzing, this resistance was used to unbalance the bridge causing a high current to be drawn from the power amplifier through the platinum foil. As a result the platinum foil heated rapidly, the resistance of the foil changed and the bridge came into balance again.

This arrangement seemed to function well, until an experiment was carried out, in which a photodiode with a short response time was placed under the foil. This arrangement was in order to determine the temperature time profile in a small area (1 mm^2) of the platinum foil (the signal from the photodiode was measured by a storage oscilloscope). It was seen that the increase in the temperature was not as fast as had been expected. Tests showed that this was due to the cooling effects of the end fastenings of the platinum foil. The resistance of the foil decreased as it cooled, the bridge became unbalanced and a compensating increase in current resulted which caused further heating in the foil. The voltage drop was constant, but the resistance decreased and the current increased with time. It was not until the temperature gradient in the foil had been stabilized that an increase in the current was prevented, thus allowing a constant temperature to be maintained. It was also noticed that the TRT was 300-400 msec which was too long.

In order to overcome this problem it was necessary to decrease the TRT. To achieve this the platinum foil was heated by two current pulses [II]. The first current pulse heated the platinum foil very rapidly, <10 msec, the second current pulse compensated for cooling effects. The TRT was dependent on the time and the amplitude of the first current pulse and could be changed from a few milliseconds upwards by lowering the amplitude. If the temperature of the surroundings changed, the pyrolysis temperature also changed. To overcome this problem the pyrolysis chamber surrounding the platinum foil was thermostated [III].

No compensation could be made for the cooling effects resulting from conductance at the ends of the foil. Instead of a slow TRT as in the Wheatstone bridge pyrolyzer (fig) a minimum and a maximum temperature of about $\pm 10^\circ\text{C}$ for about the first 400 msec was obtained in the middle of the foil where the substance to be pyrolyzed, was placed [II, fig 8]. This change in temperature could probably be compensated for at high temperatures by altering the current,

using a photodiode, but at lower temperatures this could not be achieved until an IR-responding photodiode had been invented. Temperature stability during the length of each experiment was good. The stability of the temperature after the first 400°C was about $\pm 2^\circ\text{C}$ when pyrolyzing for 2 seconds [IV, fig 1].

It is worth noting that the only time it is important to keep the temperature absolutely constant is during kinetic studies, for analytical work it is less important. The apparatus is described in detail in paper II.

Determination of the pyrolysis temperature:

It is very important to know the temperature during the course of the pyrolysis to understand the results from the decomposition of the samples. When high pyrolysis temperatures ($>600^\circ\text{C}$) are employed they should be checked with a calibrated photodiode [II, III]. Calibration of the photodiode employed in this work was carried out with thin ($\varnothing 0.08$ mm) thermocouples of iron-constantan, which were spot-welded on platinum foils. The absolute values are difficult to determine, but the method can be used to determine the absolute temperature, at high temperatures (about 900°C), to within 10°C . With the temperature calibrated photodiode the temperature time profile in the foil was measured [II].

At temperatures below 600°C a photodiode cannot be used for temperature measurement and another method had to be employed. The method used for temperature measurement below 600°C depended on the fact that the resistance of a metal is proportional to the temperature ($R_T = R_0 [1 + \alpha (T - T_0)]$). However it was not known whether the temperature within the foil, which was not homogeneous, was proportional to the applied temperature.

The resistance, of foils, was measured after 2 seconds and at the same time the temperature was measured with a separate thermocouple. It was shown that a value $\frac{R_T - R_S}{R_S}$,

was proportional to the pyrolysis temperature, where R_T and R_S measured the resistance of the foil at temperatures T and S [III]. It was shown that the thermal coefficient α was dependent on the temperature of the surroundings and the composition of the foils. This meant that a temperature calibration of the foil must be carried out each time a change was made in either the surrounding temperature or if the foil was changed. A new equation could be written:

$$R_T = R_S [1 + \gamma (T - T_S)]$$

where

R_T = the resistance of the foil when the temperature in the middle is $T^{\circ}\text{C}$.

R_S = the resistance of the foil when the temperature of the surroundings is $T_S^{\circ}\text{C}$.

γ = resistance change of the foil when the temperature in the middle changes 1°C , $\approx 0.3\alpha$.

By measuring the resistance of a foil at two temperatures a two point calibration line could be drawn [III]. One temperature was determined by the photodiode, the value of the other temperature was extrapolated from the measured chamber temperature. In this way the temperature could be determined in a large temperature interval.

To check the temperature of the foil, which had been determined by a two point calibration line, 7.4 μg cis-1.4-polybutadiene were pyrolyzed. It was shown [IV] that cis-1.4-polybutadiene was decomposed to the monomer and that the amount of monomer was proportional to the pyrolysis temperature. At high temperatures, when the reaction rate was fast, only the maximum temperature could be determined.

The systematic error in the temperature determined from the two point calibration line, has not been compensated for. The temperatures around 500°C will therefore show the greatest error and be about 8°C too high.

Influence of different pyrolysis conditions:

TRT

Much has been said about the necessity of using a short TRT [7,8] but no-one has tried to explain the difference in results obtained if a short or long TRT is used. There are probably three things which may happen:

- 1) The decomposition will change with temperature (primary effect).
- 2) The decomposition time will change.
- 3) Decomposition of primary decomposition products, (secondary effects), will occur.

Referring to these points:

the first will probably lead to a change in the amount of decomposition products, some things will decrease and some increase or new products will be formed. The second will displace all the results towards longer times and could probably be adjusted if the TRT of the pyrolyzer is known. The third will decrease the amount of all products, depending on the amount of carbonization. Or if the secondary effects result in decomposition of high boiling products to give low boiling products, the peak area of the high boiling products will decrease and the peak areas of the low boiling products will increase. The effects on the decomposition time of TRT and secondary effects (no 2 and 3) have been found to different extents when decomposing cis-1.4-polybutadiene [V], and polystyrene [VI].

Pyrolysis temperature.

When talking about pyrolysis temperature one ought to differ between two different types. One occurs when the pyrolysis temperature could be regarded as constant, that is when the TRT is short, compared to the effective pyrolysis time*. The other occurs when the decomposition takes place during the temperature rise. This is called pyrolysis to an end-temperature.

*effective pyrolysis time = that period when there is substance left to be pyrolyzed.

Probably the same three things (page 6) will also influence the results when the pyrolysis temperature is changed.

The results that were measured when the pyrolysis temperature for cis-1.4-polybutadiene was changed, suggest that the amount of sample decomposed is proportional to the temperature. The monomer peak increased with increasing temperatures up to 1000°C independently of the time. With temperatures above 1000°C secondary effects which cause changes in product composition were evident.

The same amounts of different molecular weight species of polystyrene decomposed differently with different pyrolysis temperatures. The lowest molecular weight species decomposed to oligomers to a greater extent than higher molecular weight species. When temperatures above 800°C were used, secondary effects became apparent and as in the case of polybutadiene the amount of the products changed.

Different amounts and areas of the sample.

If the amounts of sample are changed the temperature gradient within the sample is changed. The results are similar to the results that occur when the pyrolysis temperature is changed. Changes due to increase in secondary effects will also occur, when larger areas of sample are used.

When cis-1.4-polybutadiene was pyrolyzed to an end-temperature of 1000°C a temperature gradient was noted [V, fig 4]. When pyrolyzing different amounts of sample at low pyrolysis temperatures, effects, other than those caused by a temperature gradient in the sample, could be seen and they appeared to be more dominant [V, fig 6].

If the area of the same amount of sample is decreased there will be a greater temperature gradient in the sample. On the other hand the temperature gradient experienced in the foil will be less because the sample will be contained

within a smaller area. In paper V and VI different volumes of different concentrations of the two substances cis-1.4-polybutadiene and polystyrene were placed on the platinum foil and pyrolyzed at different temperatures. It was concluded that the greatest effect was due to differences caused by secondary reactions.

The effects of using different amounts and areas of the sample will be discussed later when talking about quantitative analyses.

Secondary effects.

In the literature very little has been reported about secondary effects. Jones and Moyles said [9] that if small enough amounts of substance (20 μ g) were used no difference will occur in the pyrograms if the material of the pyrolyzer is changed. If relative values, instead of absolute values, are used it is difficult to separate the secondary and primary effects. In papers IV, V and VI secondary effects have been discussed. The way of pyrolyzing the samples, discussed in paper V, could be used to show that carbonization and decomposition of butadiene to lighter hydrocarbons were secondary effects.

Although it has been suggested that, by changing from a platinum foil to another type of metal foil, most of the secondary effects can be decreased, there is insufficient evidence at present, and further experimental work, to demonstrate that this is so is currently being pursued. One possible pitfall which can be avoided when platinum is used, are reactions with the metal in the foils. Other metals are not as inert as platinum and this can be seen as changes in the resistance of the foil, which, in turn will influence the reproducibility of the pyrolysis temperatures. If reproducibility of the pyrolyses is poor, the gain due to the decrease in secondary effects will be lost.

Reproducibility requirement:

The most important of a pyrolyzer is that it reproduces

the decomposition products for each pyrolysis, not only in relative values but in absolute values. This is important when making qualitative analyses but necessary when making kinetic and quantitative studies.

When making kinetic studies on the decomposition of a sample it is pointless having short TRT:s and in maintaining an absolute temperature that is constant and known, if the decomposition products do not give reproducible values. Poor reproducibility results, if the sample cannot be exactly placed on the pyrolyzer for each pyrolysis, if the same amounts of sample are difficult to apply and if the pyrolysis temperature time profile is not reproducible.

In the work presented here it has been shown that the pyrolyzer used can reproduce the decomposition results, when pyrolyzing polymers, to within $\pm 1\%$ when the larger product-peaks are compared and to within $\pm 5\%$ for products which form only one per cent of the total amount of products [II, table I; VI, table I]. The reproducibility of products formed during the decomposition of salts was of the same order or somewhat higher [VII, table I]. Salts are much more difficult to handle in the pyrolyzer than for example polymers, they can change the composition and structure of foil where the substance is placed which will influence the pyrolysis temperature.

Kinetic studies:

Most decomposition studies of polymers have been made by thermal gravimetric analysis (TGA), but as long as the TGA apparatus is not combined with an analytical system capable of analysing the decomposition products, the only information which results is that due to weight loss of the sample.

By comparison decomposition studies, made by PGC, enable the study of product formation to be made for products which make up only a few per cent of the total amount of products formed [VI]. Samples in the μg range can be used

[IV, VI], and decomposition studies could be carried out at relatively high temperatures compared to the temperatures used in TGA [VI, table V].

For kinetic studies a new and more rapid technique was introduced, called pulse pyrolysis. In this technique the same sample is pyrolyzed successively several times at the same temperature and for the same time. The peak area of the decomposition products for each individual pyrolysis was summed as was the individual pyrolysis times. This means that the peak areas (integrator counts) of the pyrolysis products could be plotted against time, thus enabling the decomposition mechanism to be studied [IV, fig 4; VI, fig 8].

Kinetic studies of the decomposition products formed from cis-1.4-polybutadiene and from different molecular weight species of polystyrene were made. The two substances behaved quite differently during decomposition, but the rate of formation of the decomposition products from both samples was first-order [IV, fig 6; VI, fig 9,10,11,13].

Cis-1.4-polybutadiene was pyrolyzed, at an ideal TRT, between 450°C and 530°C and polystyrene between 550°C and 600°C. However polystyrene decomposition could be studied at somewhat higher temperatures than 600°C. An ideal TRT means that the TRT is small compared to the effective pyrolysis time, this means that no decomposition must take place during the TRT. For a pyrolyzer with a long TRT it means that the maximum pyrolysis temperature that can be used is lower than for a pyrolyzer with a short TRT. The minimum pyrolysis temperature is determined by the resolution of the products on the gas chromatograph column. If the injection time is too long bad resolution will be obtained. This means that there is a temperature range within which any temperature would give ideal pyrolysis conditions for decomposition studies [IV].

Qualitative analyses:

Standardizing pyrograms is probably not the best way to solve qualitative problems [VI] but the unknown sample could probably be analyzed roughly using this technique. However if suitable standard solutions were injected on the gas chromatograph the peaks from the solution and from the pyrolyzer could then be compared; for example if the sample is a polymer, a standard solution of different monomers could be injected using the same gas chromatographic conditions as those used for the unknown sample. If this technique is used the gas chromatographic and pyrolysis conditions chosen are independent of the results. If there are peaks in the unknown sample which have the same retention times as those in the reference solutions it would suggest the need for further information.

The pyrolysis conditions for qualitative studies are probably easy to deduce because most decomposition products will be formed independently of the pyrolysis conditions, it is only the peak areas from the different products, which vary [VI].

In paper I potassium salts of normal-, iso- and sec butyl xanthic acids could easily be differentiated by the separation of the decomposition products on a dinonylphthalate column.

Quantitative studies:

If the formation of decomposition products is a first-order reaction the amount formed at each time is dependent on the temperature and proportional to the amount of sample pyrolyzed.

This means that if the pyrolysis time and temperature are constant and the amount of sample is changed the amount of products formed ought to give a linear response when plotted against the amount of sample, or a value proportional to the amount, pyrolyzed.

In practice there are problems to keep the pyrolysis temperature in the sample constant and to avoid changes in the secondary effects. There is a temperature gradient along, across and through the sample. The temperature gradients along and across the sample are constant as long as the sample is positioned on the same part of the pyrolyzer. This can be done if the same volume of solution is placed on the foil and if the viscosity of the solutions are the same. One may also minimize the effect of temperature gradient in the foil by pyrolyzing at high end-temperatures reached in a short time (msec) [V, fig 4], when the cooling effects from the fastenings of the platinum foil will not have time to occur. The temperature gradient through the sample could be decreased by pyrolyzing very small amounts of sample ($\mu\text{g's}$) or could be kept constant if using nearly the same amounts.

When making quantitative analyses a pyrolysis temperature should be chosen where the pyrolysis results do not vary greatly [VI, fig 2; VII, table III] with the temperature.

Quantitative determinations of two barbituric acids in the same tablet formulation was done [VII]. The acids were converted to salts and isolated from four other components by extracting with NaOH.

First the solution was pyrolyzed to find specific peaks for the two substances and then the reproducibility of the decomposition products was estimated. To choose the right decomposition conditions, the salts were pyrolyzed at different pyrolysis temperatures and times. It was also shown that excess NaOH influenced the decomposition results.

It is important to use the same substances in the calibration solutions as in the sample solutions to get as identical pyrograms as possible. This is especially important for the start and cut off of the integrator as the peaks are not totally resolved. The reproducibility of the pyro-

lyses was good, with an error of less than $\pm 3\%$.

It was very important to clean the platinum foil in the right way in case the resistance of the foil is changed which would change the pyrolysis temperature and prevent reproducibility. Reports of the quantitative determination of salts, by pyrolysis gas chromatography, has not been found in the literature.

Conclusions:

It has been shown that the foil pulse pyrolyzer used in the papers [II-VII]:

- 1) can reproduce the peak area of the decomposition products with less than one per cent error and up to a few per cent when pyrolyzing μg of polymers and salts. It was also shown that the peak area of decomposition products which made up only a few per cent of the total amount of products formed, could be reproduced to within a few per cent.
- 2) can easily be temperature-calibrated.
- 3) can easily reproduce a pyrolysis temperature even if the platinum foil is changed.
- 4) has a known temperature time profile in the foil.
- 5) the TRT is short (8 msec) and independent of the pyrolysis temperature.
- 6) secondary effects could be determined.
- 7) can be used for qualitative, quantitative and kinetic studies of polymers and salts. Suitable pyrolysis conditions have been proposed for the three different fields.

One big drawback with the platinum foil pulse pyrolyzer is that it has been shown that there are a great many secondary effects such as carbonization of the hydrocarbons even at low temperatures, probably depending on the material in the foil. By changing the material of the foil, which has been proposed [II], secondary effects may be decreased.

The absolute calibration of the pyrolysis temperature could be better if thinner thermocouples are made and the fastenings could be controlled.

The technique of pyrolysis gas chromatography is ready to be used not only for qualitative analyses of polymers but for:

- 1) qualitative and quantitative analyses of salts,
- 2) structural studies and
- 3) studies of the decomposition rates of the different products formed.

Instead of trying to standardize pyrograms people working with pyrolysis gas chromatography should produce data, which is independent of the gas chromatographic conditions, about known substances and this data would be of great value, if it were collected, indexed and published, together with information about the pyrolysis conditions and pyrolyzers used, as a reference text for people working in the field of pyrolysis.

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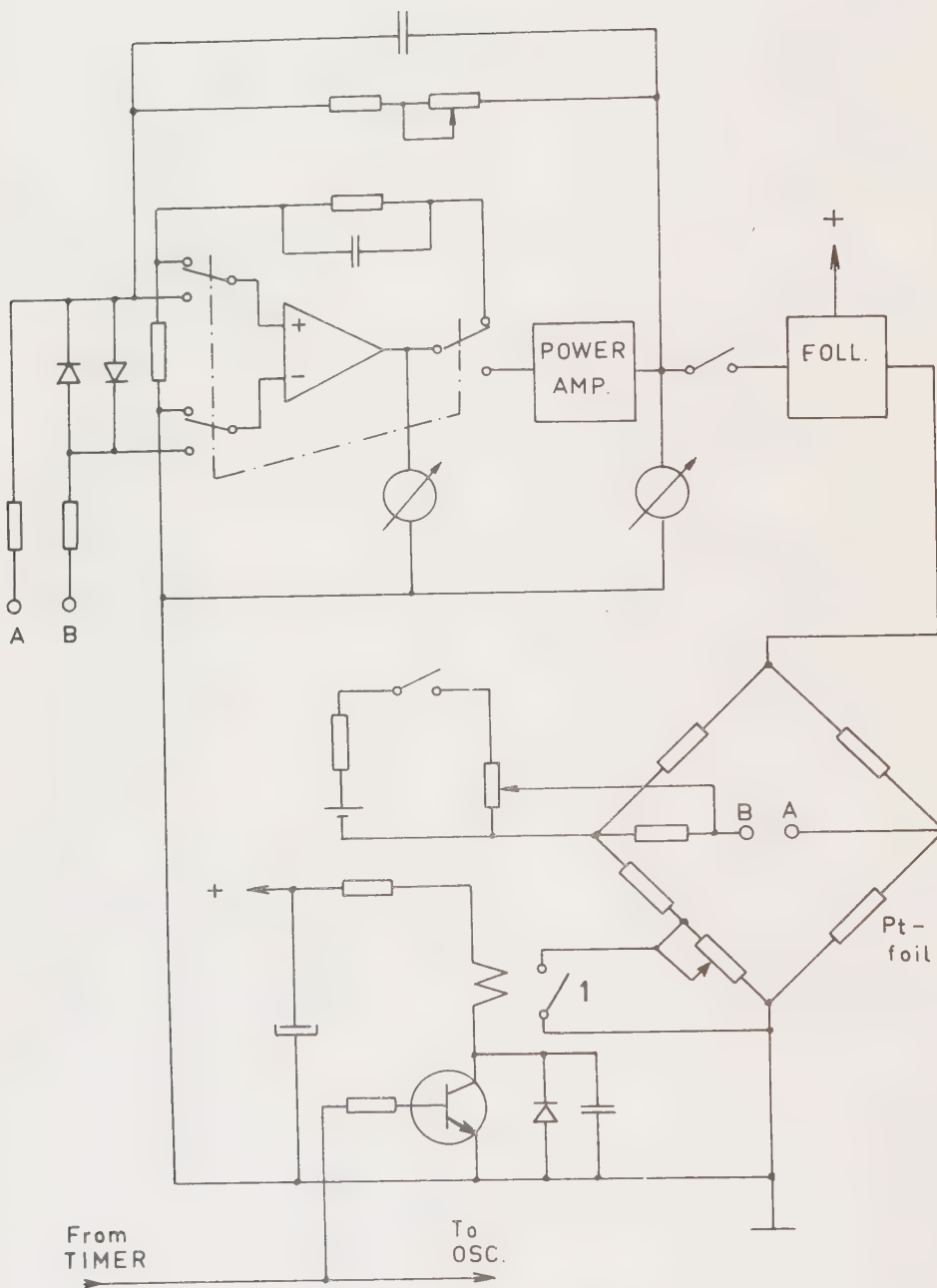


Figure: Schematic diagram of the Wheatstone bridge pyrolyzer.

GAS CHROMATOGRAPHIC STUDY OF THE PYROLYSIS OF POTASSIUM SALTS OF XANTHIC ACIDS

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Summary—A pyrolysis apparatus was developed for studies over a wide temperature range. Potassium salts of xanthic acids were pyrolysed between 200° and 1225°. The decomposition temperatures were compared with the DTA curves of the corresponding salts.

INTRODUCTION

Two types of pyrolysis apparatus are described in the literature; those using flash filament pyrolysis and those using a reactor chamber technique. Ettre and Váradi¹ discussed the advantages and disadvantages of these two techniques. They pointed out the difficulty in applying a known amount of substance to a filament. Because of this difficulty no quantitative measurements have been performed. The main disadvantage of the reactor chamber technique is that the heating of the sample is not instantaneous.

Most published work in this field relates to polymers but other chemical species have been investigated, *e.g.*, barbituric acids, which have been studied by Janák² and Nelson and Kirk.^{3,4} Janák pyrolysed up to 0.1 mg of sample on a platinum wire, and Nelson and Kirk pyrolysed about the same amount of sample in a platinum cup. Janák identified alkyl and aryl hydrocarbons whereas Nelson and Kirk found mainly nitriles.

Legate and Burnham⁵ identified various types of alkyl and aryl groups in organic phosphates and thiophosphates. They pyrolysed the salts in a reactor chamber. Perry⁶ has reviewed the literature of pyrolytic gas chromatography. In the present paper a technique is described for pyrolysing a known amount of sample in a short time. This technique combines some of the advantages of both the filament pyrolysis and the reactor chamber techniques and has been used to pyrolyse potassium salts of xanthic acids at different temperatures.

EXPERIMENTAL

Apparatus

The pyrolysis unit consists of a horizontal chamber, see Fig. 1, and a platinum sheet (28 × 8 × 0.012 mm) fastened to two 1-mm platinum wires. The wires are fused into a ground glass stopper and soldered to copper wires which are passed through a nylon plug. The chamber can be closed and the carrier gas by-passed by means of two stop-cocks. In order to prevent condensation the chamber is heated to 100° by a heating tape. The unit is connected to a glass column with a ground-glass joint (3 in Fig. 1). The platinum sheet is connected in series with a resistor, 5.5 Ω, and a push-button switch to a variable transformer. The pyrolysis products were separated in a Pye gas chromatograph employing a ²¹⁰Pb detector.

Dried argon is passed through a sampling valve⁷ to the pyrolysis unit and the gas chromatograph.

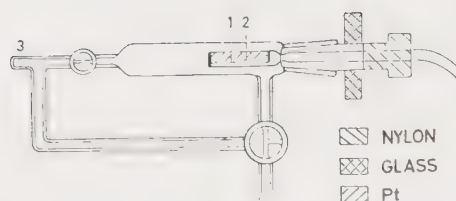


FIG. 1.—Schematic diagram of the pyrolysis device.

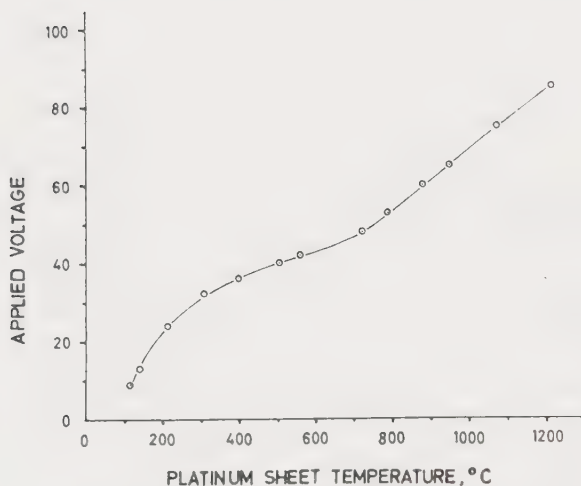


FIG. 2.—Temperature calibration of platinum sheet.

The pyrolysis products were separated on two glass columns, both 138 mm long and 4 mm inner diameter. The details for the columns are:

- (1) 15% dinonyl phthalate on 7.15 g Embacel, 60–100 mesh, inlet pressure 150 mmHg,
- (2) 16.5 g silica gel, 50–100 mesh, inlet pressure 230 mmHg.

The column temperature was 65°, the argon flow-rate 25 ml/min, and the recorder chart-speed 4 in/hr.

Procedure

A weighed amount of the salt was dissolved in distilled water. A few microlitres of solution were then taken with a Hamilton syringe and applied to the platinum sheet. The sample was spread out with the needle in the central part of the sheet (between 1 and 2 in Fig. 1).

The water was evaporated carefully by an infrared lamp, leaving a very thin film of the salt on the platinum sheet. The sheet was put into position, and the chamber was flushed with argon to remove the air. When flow equilibrium was attained current was passed through the sheet for 5 sec.

In order to remove any carbon and sulphur residues the platinum sheet was heated to redness in a Bunsen flame, washed with dilute hydrochloric acid and distilled water and then heated again. This procedure was repeated after each pyrolysis.

In all cases 0.31 μ mol (about 50 μ g) of the sample was pyrolysed. Two pyrolyses were run at each sheet temperature. A fresh sample solution was prepared for each pyrolysis. The xanthic salts investigated on the two columns were prepared at different times by known methods.⁸

Temperature calibration. The temperature of the platinum sheet was determined as a function of the applied voltage. Up to 800°, temperatures were measured by slowly increasing the voltage until samples of known compounds just melted. Above 800° an optical pyrometer, Hartmann and Braun Pyropto, was used.⁹ Figure 2 shows the result of the calibration. To check the correctness of the curve two thin platinum wires were soldered at 1 and 2 (Fig. 1). The voltage drop was measured with an oscilloscope and converted into temperature. The results were in agreement with those shown in Fig. 2.

TABLE I.—PYROLYSIS OF *n*-BUTYL POTASSIUM XANTHATE AT 1075°

Experiment No.	Peak height, % full scale						
	1	2	3	4	5	6	7
I	23	56	27	8	14	78	8
II	23	57	26	9	16	82	8
III	24	57	34	8	19	73	8
IV	25	54	30	8	15	89	8
V	24	54	26	9	15	76	7
Mean	24	56	29	8	16	80	8
Standard deviation	1	2	3	0.8	2	6	0.5
Detector voltage	1000	1000	1750	1750	1750	1750	1750

Pyrolysis sheet life and reproducibility of the pyrolyses. The lifetime of platinum coils has been discussed by Jennings and Dimick.¹⁰ They noted that the coils became brittle, and ascribed this to carbon residues in the metal.

To study the aging of the platinum sheet, an arbitrarily chosen pyrolysis was repeated after more than one year or after at least 300 pyrolyses. The peak heights were 20% lower the second time, but there was no change in the relative amounts of the different compounds formed. This decrease in the amount recovered may be explained by a decrease in the sensitivity of the gas chromatographic equipment. The cleaning of the platinum sheet between the pyrolyses may increase the lifetime so that the aging proceeds much more slowly than described by Jennings and Dimick.

In order to show the reproducibility, 5 samples of *n*-butyl potassium xanthate were pyrolysed immediately after each other. The results, in Table I, show good reproducibility of peaks 1 and 2, while the scattering is larger for the other peaks, which may be explained by the large uncertainty of the gas chromatography at this high sensitivity.

RESULTS AND DISCUSSION

Silica gel column

Potassium salts of ethyl, isopropyl, *n*-butyl and *n*-amyl xanthic acids were pyrolysed at 225, 675, 1000 and 1225°. Only gaseous compounds and carbon disulphide from the pyrolyses were separated, while liquid products were retained on the column. Calibration for the gases was made with the gas sampling valve.⁷ Carbon disulphide was diluted in pyridine and introduced with a micropipette. A short column filled with Dehydrite was put in front of the silica gel column to absorb the pyridine which has a long retention time with severe tailing. All peaks were identified by comparing their retention times with those of known substances under the same conditions. This procedure was repeated at different column temperatures to provide as positive an identification as possible. Qualitative and quantitative results of the peaks are given in Fig. 3.

The hydrogen sulphide results were not reproducible and were omitted from Fig. 3. Carbon dioxide is probably produced in the pyrolyses but it could not be detected by the apparatus used. Figure 4 shows a typical chromatogram obtained with the silica gel column.

In the pyrolyses of the four salts carbonyl sulphide and carbon disulphide were produced in nearly equal quantities. The yield of hydrocarbons, however, depended on the length of the carbon chain of the molecule.

Dinonyl phthalate column

Potassium salts of methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl and sec-butyl xanthic acids were pyrolysed between 200 and 1075°. The gas chromatograph had no temperature programming facilities so the peaks were very close in the first

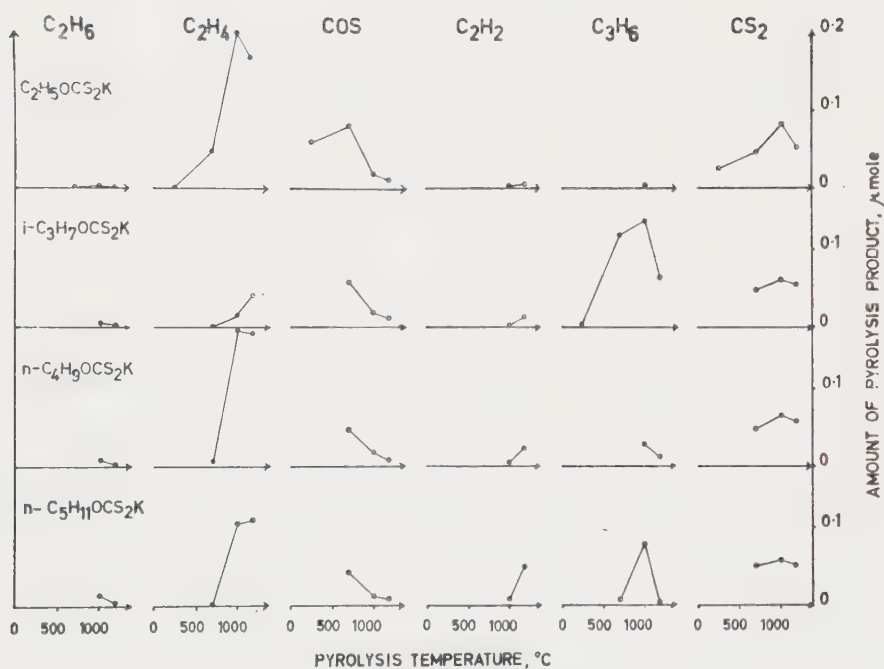


FIG. 3.—Compounds formed by pyrolysis of potassium salts of xanthic acids at 225, 675, 1000 and 1225°.

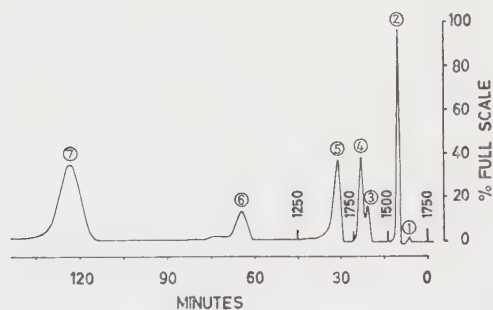


FIG. 4.—Typical chromatogram obtained from pyrolysis of 0.31 μ mole of iso- $\text{C}_3\text{H}_7\text{OCS}_2\text{K}$ at 1225°.

Peaks:

1. Ethane, 2. Ethylene, 3. Carbonyl sulphide, 4. Acetylene, 5. Hydrogen sulphide,
6. Propylene, 7. Carbon disulphide.

part of the chromatogram; the base line position was dependent on the sensitivity. Because no quantitative evaluation was planned originally, the highest sensitivity range which still gave a stable base line was used all the time to get patterns of the salts. For these reasons, most of the peaks were so high that their tops were cut off. Afterwards a rough estimation of the amount of substance produced was made by measuring the peak widths at full scale of the recorder, 100%. When the

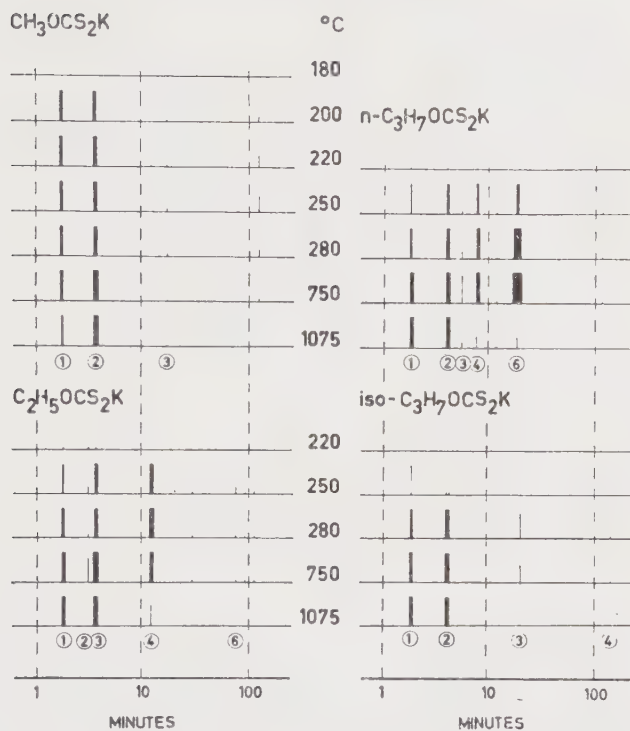


FIG. 5.—Gas chromatographic separation of pyrolysis products of potassium salts of xanthic acid.

$\text{CH}_3\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons + CH_3SH , 2. CS_2 + CH_3OH + $(\text{CH}_3)_2\text{S}$, 3. $(\text{CH}_3)_2\text{S}_2$; $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. $\text{C}_2\text{H}_5\text{SH}$, 3. CS_2 + $\text{C}_2\text{H}_5\text{OH}$, 4. $(\text{C}_2\text{H}_5)_2\text{S}$, 5. $(\text{C}_2\text{H}_5)_2\text{S}_2$; $\text{n-C}_3\text{H}_7\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. CS_2 , 3. $\text{n-C}_3\text{H}_7\text{SH}$, 4. $\text{n-C}_3\text{H}_7\text{OH}$, 6. $(\text{n-C}_3\text{H}_7)_2\text{S}$; $\text{iso-C}_3\text{H}_7\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. CS_2 + $\text{iso-C}_3\text{H}_7\text{SH}$ + $\text{iso-C}_3\text{H}_7\text{OH}$, 3. $(\text{iso-C}_3\text{H}_7)_2\text{S}$?, 4. $(\text{iso-C}_3\text{H}_7)_2\text{S}_2$.

peaks did not reach full scale the percentage of full scale was measured. These estimations will give a semi-quantitative measure of the changes due to changed pyrolysis temperatures. As the detector response depends on the nature of the substance and as the peak width depends on the retention time, it is not possible to evaluate a quantitative relation between different pyrolysis products or different salts. In Figs. 5 and 6 the percentage of full range or the peak width as defined above is plotted *vs.* the logarithm of the retention time. A typical chromatogram obtained on the dinonyl phthalate column is shown in Fig. 7.

All salts produce carbonyl sulphide, carbon disulphide, mercaptans and alcohols and probably aldehydes, sulphides and disulphides. Peak 1, Figs. 5 and 6, contains all the gaseous compounds produced. Most of them were identified on the silica gel column (Fig. 4). This peak increased with increasing temperature except for the methyl salt where carbonyl sulphide and methyl mercaptan were the main products. In the other cases the hydrocarbons were dominant depending on the longer hydrocarbon chain. In these cases the mercaptans were separated from peak 1 which reduced the dominance of this peak.

The aldehydes could only be identified for n-butyl and s-butyl xanthates but

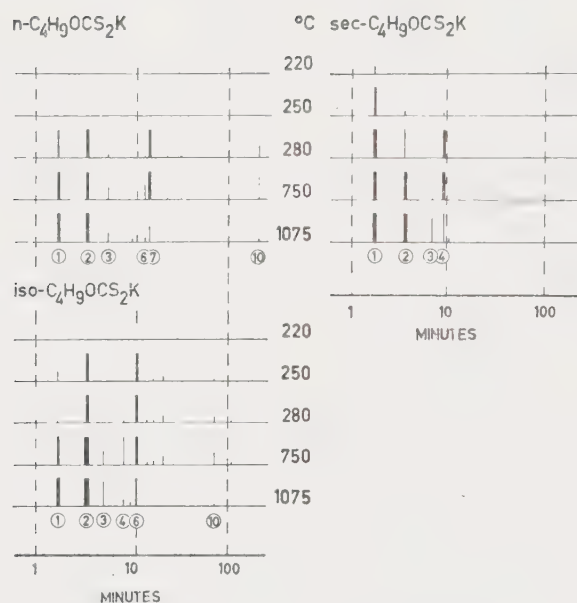


FIG. 6.—Gas chromatographic separation of pyrolysis products of potassium salts of xanthic acid on a dinonyl phthalate column.

$n\text{-C}_4\text{H}_9\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. CS_2 , 3. $n\text{-C}_3\text{H}_7\text{CHO}$, 6. $n\text{-C}_4\text{H}_9\text{SH}$, 7. $n\text{-C}_4\text{H}_9\text{OH}$, 10. $(n\text{-C}_4\text{H}_9)_2\text{S}$; $s\text{-C}_4\text{H}_9\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. CS_2 , 3. $s\text{-C}_4\text{H}_9\text{SH}$, 4. $s\text{-C}_4\text{H}_9\text{OH}$; $s\text{-C}_4\text{H}_9\text{OCS}_2\text{K}$, 1. COS + light hydrocarbons, 2. CS_2 , 3. $\text{iso-C}_3\text{H}_7\text{CHO}$, 4. $s\text{-C}_4\text{H}_9\text{SH}$, 6. $s\text{-C}_4\text{H}_9\text{OH}$, 10. Unidentified.

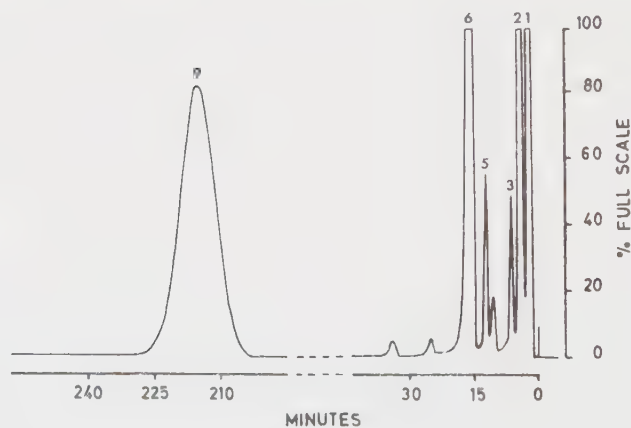


FIG. 7.—Typical chromatogram obtained from pyrolysis of $n\text{-C}_4\text{H}_9\text{OCS}_2\text{K}$ at 750° . Peaks; 1. COS + light hydrocarbons, 2. CS_2 , 3. $n\text{-C}_3\text{H}_7\text{CHO}$, 5. $n\text{-C}_4\text{H}_9\text{SH}$, 6. $n\text{-C}_4\text{H}_9\text{OH}$, 9. $(n\text{-C}_4\text{H}_9)_2\text{S}$

TABLE II.—DECOMPOSITION TEMPERATURES OF XANTHATES

Sample	T_P°	T_{DTA}°	T_{lit}^{**}
CH_3OCS_2K	180–200	165–185	182–6
$C_2H_5OCS_2K$	220–250	210–225	225–6
$n-C_3H_7OCS_2K$	220–250	220–240	233–9
$i-C_3H_7OCS_2K$	220–250	230–275	278–82
$n-C_4H_9OCS_2K$	250–280	235–255	255–6
$i-C_4H_9OCS_2K$	220–250	250–265	260–70
$sec-C_4H_9OCS_2K$	220–250	220–260	

* T_P = the temperature interval in which the pyrolyses start. It is read from Figs. 5 and 6
 T_{DTA} = the DTA decomposition temperature. The interval is taken from the start to the end of the transition
 T_{lit} = literature values¹¹ of the decomposition temperature

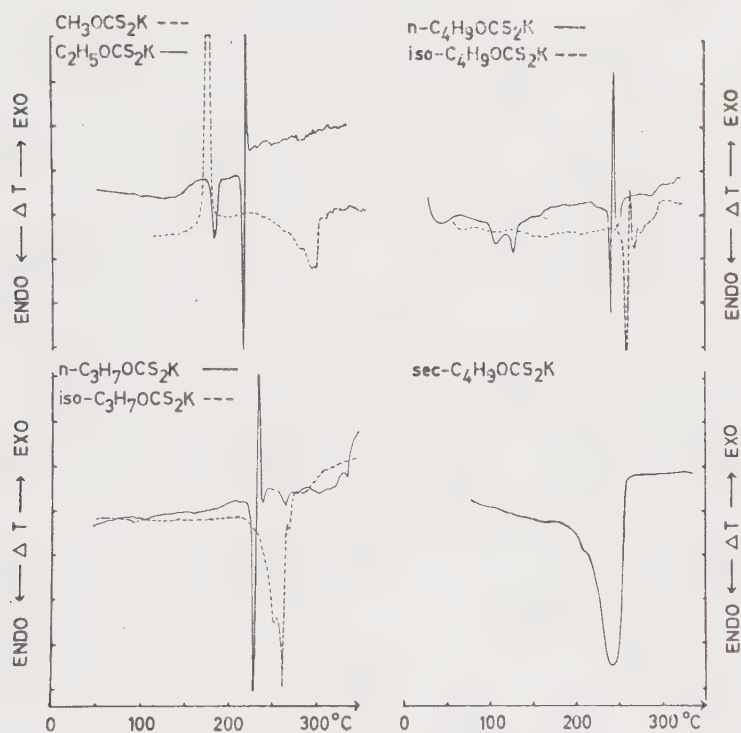


FIG. 8.—DTA curves of xanthates.

not for the other xanthates because the aldehydes do not separate from the carbon disulphide peak or from peak 1. The monosulphides could be positively identified only for the methyl, ethyl and *n*-butyl salts, as the other sulphides were not available. When the logarithms of the retention time for the homologous series of normal sulphides were plotted *vs.* the number of carbon atoms a straight line was obtained. The logarithm of the retention time for peak 6 fell on this line which suggests that the peak corresponds to *n*-dipropyl sulphide. The monosulphides from isopropyl and

s-butyl xanthates are supposed to be peak 3, and peak 10, respectively. The monosulphide from s-butyl xanthate was probably produced in too small an amount to be detected. The disulphides have too long a retention time to be detected within reasonable time except for dimethyl disulphide, diethyl disulphide and isopropyl disulphide. The n-xanthates form monosulphides more readily than the iso- and s-xanthates, probably because the iso- and s-hydrocarbon chains decompose more easily to smaller components. The amounts of mercaptans and alcohols as well as the amounts of monosulphides and disulphides decrease with increasing temperature.

Some of the xanthates pyrolysed were investigated by differential thermal analysis by means of the Du Pont 900 DTA instrument. This provided an additional and independent check on the decomposition temperatures. The thermograms and operating conditions are shown in Fig. 8, and a comparison of the results obtained by different methods is given in Table II.

Acknowledgement—The author is greatly indebted to Professor K. J. Karrman for helpful and stimulating discussion concerning this work. She would also like to thank Docent G. Johansson and Dr. L. Haraldson for their interest and great help.

Zusammenfassung—Ein Pyrolyseapparat zu Untersuchungen in einem weiten Temperaturbereich wurde entwickelt. Kaliumxanthate wurden zwischen 200 und 1225° pyrolysiert. Die Zersetzungstemperaturen wurden mit den DTA-Kurven der entsprechenden Salze verglichen.

Résumé—On a élaboré un appareil à pyrolyse pour études dans un large domaine de températures. On a pyrolysé des sels de potassium d'acides xanthiques entre 200° et 1225°. On a comparé les températures de décomposition aux courbes ATD des sels correspondants.

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Summary

A pyrolyzer of improved design for control of pyrolytic conditions and incorporating facilities for varying different parameters has been constructed to permit examination of the variability of pyrolysis under different pyrolytic conditions. Very good absolute reproducibility has been achieved, which now makes it possible to assess such factors as sample size, surface area and thickness.

Introduction

Pyrolysis gas chromatography has long been recognized as a useful technique for the characterisation of polymeric materials and non-volatile substances. Its usefulness is limited by difficulties in standardizing the pyrolysis conditions sufficiently to obtain reproducible results from different pyrolyzers. Ideal conditions, requiring instantaneous heating of the whole substance to a well-defined temperature without development of secondary reactions due to influence from the surroundings, would in most cases give a well-defined pyrolysis. Such ideal conditions cannot even be approached in practice. For that reason it is instructive to see how results are influenced by deviation of pyrolysis parameters from ideality.

The following need to be defined to characterize the pyrolytic conditions well enough for inter-laboratory comparisons:

1. Temperature rise time and cooling time.
2. Temperature and temperature gradient where the substance is located.
3. Quantity and surface area of the test substance.
4. The effective pyrolysis time, which means that the selected pyrolysis time must be corrected to include only that period when there is substance left to be pyrolyzed.
5. Material and nature of sample holder.
6. Conditions of the surroundings, eg. nature of carrier gas, carrier gas flow, volume and temperature.

Data for 1 and 2 must be accompanied by information about the method of measurement, and reproducibility obtained on pyrolysis must be stated.

This work constitutes the first part of a project with the purpose of investigating the influence of these six parameters on qualitative and quantitative pyrolysis gas chromatography.

For this undertaking a pyrolyzer was constructed such that:

1. the temperature-rise time was variable between 8 and 80 msec, independent of the final temperature,
2. a photodiode for controlling rapid temperature variations on a small area of metal sheet was employed,
3. different materials and volumes for the pyrolysis chamber could be chosen,
4. the material and dimensions of the pyrolysis foil could be varied in a simple way,
5. locating the test substance in a reproducible way on the sample holder and in relation to the walls of the surrounding chamber was possible, and
6. any pyrolysis time between 8 msec and 1 min could be selected.

The pyrolyzer was developed from a unit described in an earlier publication [1]. Although the reproducibility of this apparatus was very good, the temperature rise time was too long and uncontrollable.

Experimental

Apparatus

The new version of the pyrolyzer consists of a pyrolysis unit with chamber and a piece of metal foil mounted on a holder, and an electronic unit which produces two current pulses through the foil. The pyrolysis unit is shown schematically in Fig. 1a and b. The platinum foil; $0.012 \times 2.6 \times 15$ mm (1) Fig. 1a, can be replaced by other materials, eg. Nb, Ta or W. The metal foil is fastened on the holder at each end between two platinum-plates 1 mm thick (2). The two plates are screwed together and one is mounted on a platinum-rod (3), 1.5 mm diameter.

The two platinum-rods are connected to contacts made of brass (4), which are connected to the outer leads with threaded contacts. Because currents up to 60A are used adequate contact surface is essential. The carrier gas tubing from a three-way valve (5) is connected by means of a luer lock (6) to the foil holder.

Different foil dimensions have been examined in order to optimize performance. It was found that a foil; $0.012 \times 2.6 \times 15$ mm gave the best results. Thinner foils were easily deformed, resulting in very poor reproducibility in pyrolytic determinations. Thicker foils could be used, but these resulted in no improvement in performance and had the disadvantage of greater current consumption. The length and width were chosen to give sufficient area for application of the sample without appreciable temperature gradient.

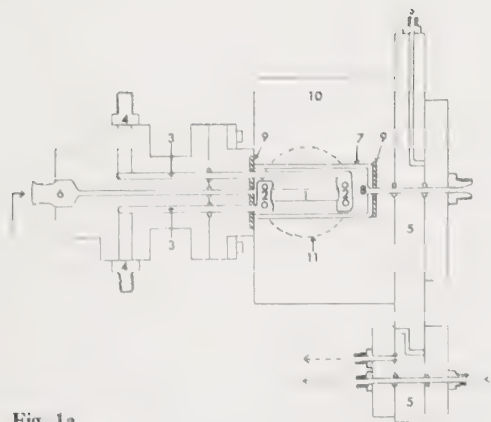


Fig. 1a

- Schematic of the pyrolysis unit, seen from above.
- 1. Platinum-foil 0.012 x 2.6 x 15 mm.
- 2. Two 1 mm thick platinum plates compressed with two screws.
- 3. Platinum-rod 1.5 mm diameter.
- 4. Brass contact
- 5. Three-way valve.
- 6. Luer lock fitting for carrier gas inlet.
- 7. Replaceable cell 24 x 10 x 5 mm inner dimensions, made of quartz, glass or Teflon.
- 8. Outlet for carrier gas to GC-column.
- 9. Viton-packing.
- 10. Aluminum chamber 35 x 50 x 50 mm.
- 11. Hole drilled in the chamber to let light from metal foil pass to photodiode.

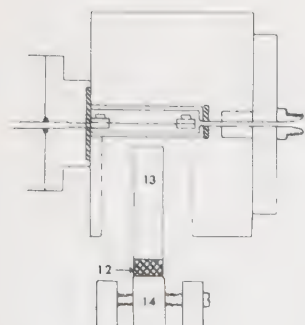


Fig. 1b

- Schematic of the pyrolysis unit, seen from the side.
- 12. Photodiode.
- 13. Cover for photodiode.
- 14. A "cross" for moving photodiode across and along metal foil.

The metal foil with holder is positioned in a cell (7) with a hole drilled in the bottom (8) for passage of the carrier gas. The inner dimensions of the cell are 5 x 10 x 25 mm. Cells of different materials can be used, such as glass, quartz and Teflon. At each end of the cell is a Viton-packing (9). The cell is surrounded by an aluminum chamber (10) which can be heated to 250 °C with a heating cartridge. In the chamber a hole was drilled (11) to locate a photodiode (12) with cover (13), Fig. 1b, and to allow light from the metal foil to pass to the photodiode.

The chamber is provided with a three-way valve (5) with two positions. In the position in Fig. 1a, the carrier gas passes through the pyrolysis unit to the column. When the sliding bar is in the lower position carrier gas by-passes the pyrolysis unit directly to the column. The temperature range for the unit is limited by the Viton-O-rings in the three-way valve, which can be used from -45 °C to +250 °C. The outer dimensions of the chamber are 35 x 50 x 50 mm. A Varian 1860 gas chromatograph, was used and the pyrolysis unit was mounted on the chromatograph replacing one of the injectors. A Servogor RE 511 recorder was used and quantitative evaluation of the peaks was made with a Varian 480 Integrator.

In order to determine very rapid changes of temperature in the foil, a photodiode HP 4220 (12) was mounted under the chamber. The photodiode was placed on a graduated "cross" (14) and was surrounded by a cylindrical cover of polypropene with a 1 mm² opening towards the foil (13). With this arrangement the photodiode can be used for monitoring the temperature along and across the foil. The area from which the photodiode will register the temperature is about 1 mm². A photomultiplier [2] and a photodiode [3] have been used earlier for temperature measurements but in these arrangements the average temperature over the entire length of a platinum-filament was measured.

For measurement of the fast signal from the photodiode, a Tektronix 564 Storage Oscilloscope was used, with type 3A3 and 3B3 as base components. For calibration of the photodiode with respect to temperature, ferroconstantan thermocouples, Teflon-insulated, 0.08 mm diameter, and Pt/Pt, Rh (10 %) thermocouples, 0.1 mm diameter, were used. The thermocouples were carefully spot-welded to the central part of the foils. An Aga Thermovision camera was used for qualitative determination of temperature gradients in the foil.

A block diagram of the electronic unit is seen in Fig. 2. The electronic unit produces two square pulses with variable time and amplitude. The first pulse is variable

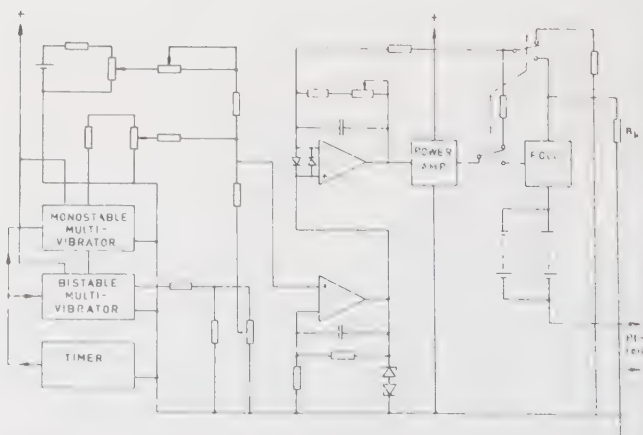


Fig. 2

- Schematic of electronic unit which heats platinum foil with two square pulses.

between 8 and 80 msec and is used for heating the metal foil to the desired pyrolysis temperature. The second pulse compensates for cooling effects and the duration can be varied by a timer from a period equal to the first pulse up to one minute.

Working Conditions

Reproducibility Test

Polybutadiene was pyrolysed at 440 °C. The duration of the first pulse was 8 msec. The effective pyrolysis time was 900 msec. 1 μ l samples of a solution containing 7.4 μ g polybutadiene per μ l were applied to an area of 6 mm² in the centre of the platinum foil with a 1 μ l Hamilton syringe and the toluene solvent evaporated. The platinum foil was "burnt off" in a bunsen flame after each pyrolysis. Pyrolysis products were separated on 15 % Apiezon on 80–100 mesh Chromosorb DMCS in a 2 m column at 150 °C. The carrier gas flow-rate was 20 ml nitrogen/min and a FID detector was used. The temperature of the aluminium chamber was 110 °C.

Determination of the Pyrolysis Temperature

The measurements with thermocouples spot-welded to the foil were made at the end of pyrolyses with 2 sec duration. These calibrations were made without sample present. With this method stable values could be obtained both from the thermocouple and the photodiode. The resistance of the metal foil can be used for determination of the pyrolysis temperature, therefore the voltage drop was also measured and a value proportional to the current was obtained by measuring the voltage drop across a constant resistance, R_k in Fig. 2, in series with the foil. Thus a value $k \cdot R$ proportional to the resistance of the metal foil is obtained by dividing the voltage drop across the metal foil by the voltage drop across the constant resistance R_k .

Results and Discussion

Time for heating and cooling

Because thermocouples have been used earlier [3, 4], some initial studies were conducted to re-assess their performance in measuring the temperature-rise time. From these investigations, it was found that the thermal response time was much too sluggish (Fig. 3) in spite of the fact that great care was taken to keep the entire welded part of the thermocouples as close to the foil as possible without risking a voltage drop between the levels.

In contrast to the response time of thermocouples, investigations with the photodiode showed that the temperature-rise time is rapid and about as long as the first current pulse, Fig. 4, providing the amplitude of the first pulse is properly chosen. As the pyrolyzer is now built, the rise-time can be assigned any value between 8 and 80 msec. The rise-time can be freely chosen regardless of the final temperature.

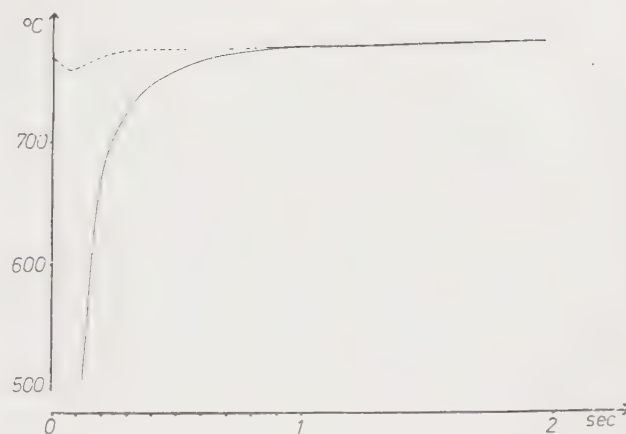


Fig. 3

- Temperature-time profiles from platinum foil measured with thermocouple (—) and with photodiode (---).

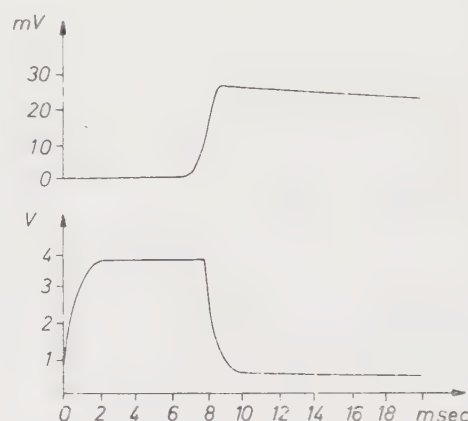


Fig. 4

- Upper curve shows initial part of response of photodiode for same pyrolysis as in figure 3. Lower curve shows voltage across a constant resistance, R_k , see Fig. 2. This voltage is proportional to current through platinum foil.

The cooling time depends on the heat content of the foil and on the heat conduction to the foil holder and to the carrier gas. The heat in the foil is determined by final temperature, mass and material, and the heat conduction by mass and temperature of the foil holder and flow rate and temperature of the carrier gas.

Measurements with the photodiode showed that cooling from 1100 °C to 600 °C takes place in 100 msec.

Determination of the pyrolysis temperature

Several platinum foils with spot-welded thermocouples were used for determination of the pyrolysis temperature on the foil under the pyrolytic conditions.

It was found difficult to achieve a reproducible calibration. If the metal foil with holder and thermocouple was taken out of the cell and reinserted, the values from the thermo-

couple would differ from earlier measurements. It seems that the orientation of the thermocouple was changed, resulting in its exposure to different temperature gradients. Measurement with the thermocouple on one platinum foil indicated temperature variations of about $\pm 10^\circ\text{C}$, and the total error including change of foils and type of thermocouple was estimated to about $\pm 20^\circ\text{C}$.

It is not practicable to calibrate each platinum foil with a thermocouple. For this reason the photodiode was calibrated against a thermocouple at different temperatures, see Fig. 5. The photodiode is not useful at temperatures lower than about 600°C , therefore another method has to be used below this temperature.

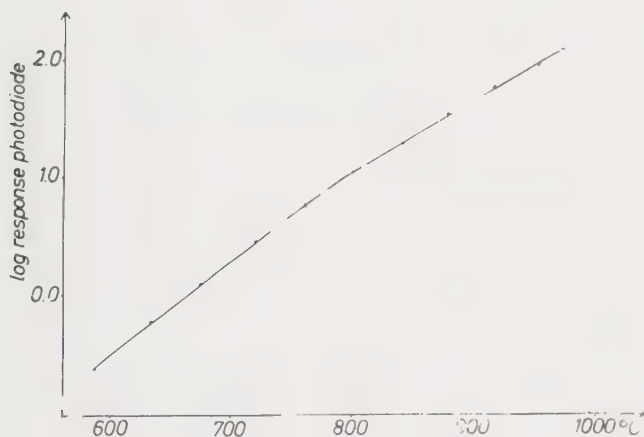


Fig. 5

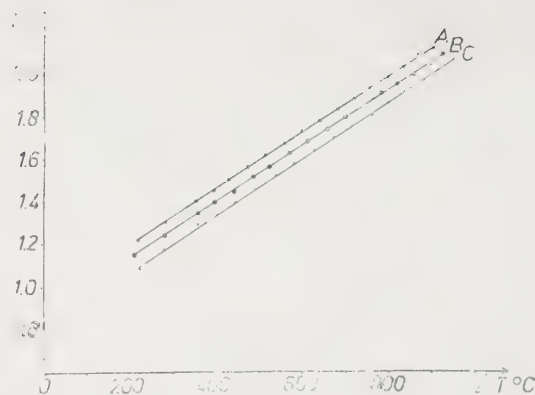
- Calibration of photodiode response against temperature of platinum foil as measured with a thermocouple.

If $k \cdot R$ is plotted against ΔT for different temperatures in the chamber, where ΔT is the pyrolysis temperature minus the temperature of the chamber T_0 , nearly straight lines will be obtained, see Fig. 6. This aspect will be discussed fully in a future publication.

Temperature gradient in the foil

The calibrated photodiode was used to study the temperature gradient in the foil. Various locations (30) on the foil have been studied in detail according to variations of the temperature with time. At ten intervals along the foil with spaces of 1 mm between them measurements were made at three points, one in the centre of the interval and the other two 0.65 mm at each side of the centre. During each such measurement the temperature time profile was taken both for a pyrolysis which lasted for 2 seconds and for a pyrolysis without sample on the foil. The final temperatures in these pyrolyses have been used to map the temperature gradient in the foil, Fig. 7.

From the figure it is evident that if a substance is applied on an area of 4 mm^2 in the middle of the metal foil, most of the substance should be pyrolysed at 910 to 918°C . The greatest variations in temperature appears at the edges of the foil.

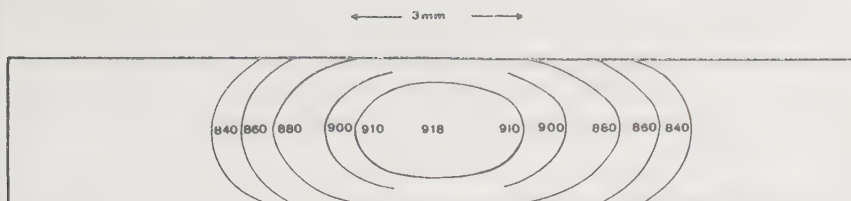


$k \cdot R$ against ΔT for different values of T_0 . $k \cdot R$ is proportional to resistance across platinum foil and $\Delta T = T - T_0$ where T is pyrolysis temperature and T_0 temperature of chamber.

A = 101°C
B = 64°C
C = 25°C

A foil was also studied with an infrared camera (Aga thermovision). The foil was not placed in the pyrolysis unit but in a glass tube and heated with constant current for a longer time than that used in the previous experiment. Temperature profiles similar to those in Fig. 7 were obtained but it was not possible to determine the absolute temperatures with this method.

Fig. 8 illustrates the temperature-time curves at two different locations on the foil. The upper curve was obtained at the centre of the foil and the lower curve 5 mm from the centre, leaving a distance of only 2.5 mm to the end with the large mass platinum plates. The first pulse was 8 msec and gave an initial temperature rise to 780°C at both locations. It is interesting to note that there is no difference in initial temperature, indicating that heat conduction to the foil holder is too slow to influence the result during this short period. After the initial pulse had ceased energy was continuously supplied by means of the second current pulse which was chosen to keep the temperature of the central part of the foil at 780°C . Due to the heat leak to the platinum plates the temperature at the location 5 mm from the centre slowly decreased until temperature equilibrium was finally reached at ca. 660°C after 300–400 msec. The heat flow towards the ends of the foil being greatest at the beginning of the second current pulse also caused a slight decrease of the temperature at the centre of the foil during the first 50 msec. The magnitude of this temperature decrease was 10 – 20°C depending on the exact adjustment of the first current pulse. The curves in Fig. 8 were obtained with a high adjustment giving a small decrease but also a following overshoot by about 10°C before equilibrium was obtained. Cf. Fig. 3 where a lower adjustment resulted in a greater decrease but with no overshoot.



Figs. 7

- Temperature profiles in a platinum foil 0.012 x 2.6 x 15 mm at the end of a pyrolysis of 2 sec duration without sample.

The cooling effects of the end-points must appear in all pyrolysis units that use a metal filament or a metal foil.

In units where the pyrolysis temperature is controlled by the voltage drop across the metal foil the cooling effects are compensated by increasing the current. This means that the temperature in the centre of the foil increases during the temperature stabilizing time of about 300–400 msec.

One possible way to compensate for the cooling effects would be to control the temperature in the centre of the foil with an IR-sensitive photodiode which controls the current through the foil.

Reproducibility

In order to analyse the reproducibility during pyrolysis, 7.4 μ g polybutadiene was pyrolysed at 440 °C. Polybutadiene was chosen only with one aspect to give a reproducible application on the Pt-foil.

Complete separation of the pyrolysis products was not attained, see Fig. 9. The main problem was to decrease the errors from the gas chromatograph and the integrator.

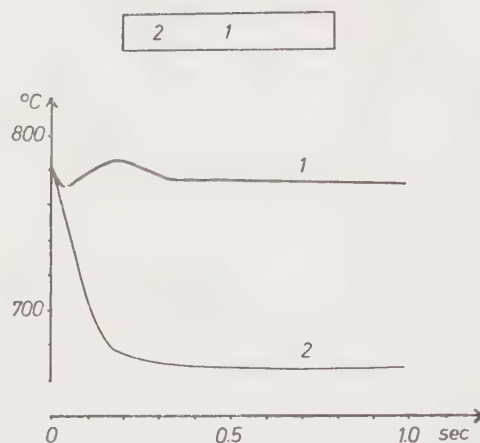


Fig. 8

- Temperature-time profiles at two different points on platinum foil.
No. 1 measured in centre of foil
No. 2 measured 5 mm from centre

Table 1. Reproducibility of peaks obtained from 7.4 μ g polybutadiene pyrolysed at 440 °C for 900 msec

Peak No.	1	2	3	4	5	6	7	Total counts
R_f	71 s	117 s	134 s	156 s	179 s	213 s	244 s	
Run No.								
1	390.9	4.891	20.35	6.016	22.61	23.22	206.9	674.9
2	391.7	4.736	19.96	5.967	22.34	22.95	206.1	673.8
3	396.8	5.011	20.55	6.068	22.67	23.11	207.8	682.0
4	393.7	4.922	20.35	5.989	22.82	23.27	197.8*	668.9*
5	384.4	4.625	19.63	5.905	21.88	22.76	203.5	662.7
6	389.5	4.878	19.92	6.023	22.31	23.02	205.6	671.2
7	392.2	4.765	20.33	5.856	22.00	22.69	195.7*	663.5*
$\bar{x}$	391.3	4.833	20.16	5.975	22.38	23.00	206.0	672.9
S %	0.98	2.7	1.6	1.2	1.6	0.96	0.79	1.0
n	7	7	7	7	7	7	5	5

R_f = retention times for different pyrolysis products.

Integral counts are all divided by 1000.

S % = standard deviation in % of mean value.

$\bar{x}$ = mean value.

n = number of pyrolyses

Peak 1 = butadiene.

Peak 2 = vinylcyclohexene.

* In these cases adjustment of integrator was poor causing premature interruption of the integration. Values are not included in calculation of standard deviation.

Table 2. Reproducibility in relative values with sum of all peaks taken as 100 %

Peak No.	1	2	3	4	5	6	7
$\bar{x}$	58.05	0.7174	2.984	0.8910	3.323	3.420	30.61
S %	0.19	2.2	0.92	0.47	0.54	0.64	0.31
n	5	5	5	5	5	5	5

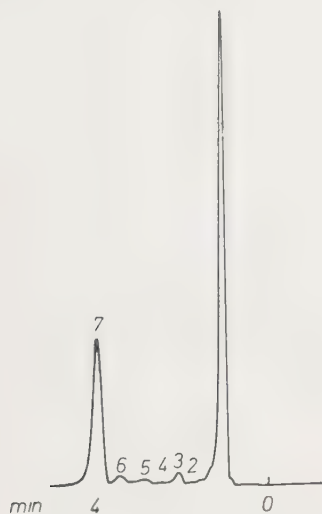


Fig. 9

- 7.4 μ g polybutadiene pyrolysed at 440 °C. Column: Apiezon 15 %, 2 m, 150 °C. Carrier gas flowrate: 20 ml/min.

It is very important to have a column with a steady baseline and to wait until all substances have emerged from the column. In this case it was one hour between each pyrolysis. One way of solving the problem was to have a constant temperature back-flush valve for the carrier gas, the time between pyrolyses could then have been decreased.

Results from seven pyrolyses are seen in Table 1. The integral counts for the different peaks are divided by 1000. These values for seven peaks with retention values, R_f , are noted in Table 1.

In the pyrolyses No. 1 and No. 7 the last peak, No. 7, was cut too early by the electronic integrator. The measured area of peak No. 7 was therefore too low and hence only five values were used for calculation of the standard deviation.

In Table 2 the results are presented as relative values with the sum of all peaks taken to be 100 %.

7.4 μ g polybutadiene was also pyrolysed with two slightly different values of the current pulses corresponding to temperatures about six degrees lower and six degrees higher than the earlier value of 440 °C. The variations in the pyrograms obtained when compared to the values in Table 1 showed that the total temperature variation was not more than ± 1 °C between the seven pyrolyses in the reproducibility test.

Acknowledgement

The author wishes to thank Dr. Lars Haraldson for valuable discussions concerning this work.

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TEMPERATURE CALIBRATION OF A PLATINUM FOIL FOR PYROLYSIS GAS CHROMATOGRAPHY.

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Summary:

The present work demonstrates 1) that it is possible and relatively easy to calibrate the temperature over a wide range for a foil pulse pyrolyzer; 2) that it is necessary to recalibrate the platinum foil when the temperature of the surroundings is changed; 3) that it is possible to reproduce the pyrolysis temperature with a new foil to within 2°C; 4) and that the temperature rise time (TRT) can be reproduced at low temperatures where a photodiode has no response. The resistance of the foil and a temperature calibrated photodiode are used; the temperature and TRT are checked by pyrolyzing polybutadiene.

Introduction:

In pyrolytic studies, it is of importance to know the temperature in the regions, on the foil where the substance is located during the course of the pyrolysis. When the temperature cannot be determined, a large store of information is lost; in addition, the standardization of pyrolyses necessitates precise temperature calibration.

A number of authors have pointed out the difficulties involved in measuring the pyrolysis temperature [1,2,3]. Perry [4] states that it is considerably easier to

measure the temperature for an oven unit than for a flash pyrolysis unit. When the Curie point pyrolyzer was introduced [5], it was anticipated that the temperature problems would be eliminated; unfortunately, these hopes were not fulfilled [6].

In this publication, which describes work in which the pyrolyzer consists of a platinum foil, the calibration of the foil will be made by its resistance and a temperature-calibrated photodiode. The aim of this publication is to show 1) that it is possible to temperature calibrate platinum foils very precisely; 2) that the foil must be recalibrated if the temperature of the surroundings is changed; 3) that it is easy to return to the same pyrolysis temperature (within 2°C) after changing the platinum foil; 4) how the temperature rise time (TRT) can be reproduced and checked at low temperatures.

In a previous publication [7], the time dependence of the temperature and the temperature variations within a platinum foil of the same dimensions as used here were discussed.

For pyrolytic work, two methods for measuring temperatures [8] are commonly used. One is to observe the melting of a salt of known melting point [9,10,11] and the other is to measure the temperature by means of a thermocouple spot-welded to a filament or foil [6,7].

To be able to recognize the melting of a small amount of substance a microscope is necessary, placed in such a fashion that the melting of the salt occurs in the same way as during the pyrolysis. Since this is extremely difficult to carry out in practice, and since it is also difficult to combine the time when the salt melts with the temperature profile, the thermocouple method was chosen.

Experimental:

Apparatus.

The pyrolyzer basically consists of a platinum foil heated by two current pulses and has been described in detail elsewhere [7]. A thermostat for temperature control of the pyrolysis chamber has been added to this previously described apparatus.

For temperature measurement, 0.08 mm teflon insulated iron-constantan thermocouples were used. The thermocouple leads were taken out through a rubber membrane in a side arm at the carrier gas inlet. The thermocouples were spot-welded to the upper side of the platinum foil, so they would not hinder light from passing to a photodiode placed under the foil.

When measuring the temperature in the middle of a platinum foil, the foil, with a spot-welded thermocouple, was placed in the glass-cell in the same position as if it were for a pyrolysis experiment. The platinum foil was heated, and, after two seconds, the voltage drop over the platinum foil and over a constant resistance R_k [7, fig 2] was measured, as were the voltages produced by the photodiode and the thermocouple. The ratio between the voltage drop across the platinum foil and voltage drop across the constant resistance, R_k , gives a value proportional to the resistance of the platinum foil, $k \cdot R_T$. If the platinum foil is not heated, the value proportional to the resistance is $k \cdot R_S$. Voltage measurements were made using model 1820 Eldorado digital voltmeters and the signal from the photodiode was measured with either a Tektronix 564 Storage Oscilloscope or a Servogor RE 511 recorder.

Sample preparation and working conditions.

14.8 mg Polybutadiene (Cariflex 1220 (Shell Chemicals), containing 96.5% cis-1.4-butadiene) was dissolved in 2 ml of toluene and 1 μ l of the solution was positioned on the platinum foil using a 1 μ l Hamilton syringe. Most of the toluene was evaporated before placing the pyrolyzer in

the glass-cell. The gas chromatographic conditions were the same as in an earlier publication [7].

Results and discussion:

Estimation of the pyrolysis temperature in the middle of the platinum foil.

For metals a temperature variation will cause a change in the resistance, which obeys the following equation:

$$R = R_0 [1 + \alpha (T - T_0)] \quad (1)$$

In this expression,

R = the resistance at $T^{\circ}\text{C}$

R_0 = the resistance at $T_0^{\circ}\text{C}$

α = the temperature coefficient

Over a large temperature interval Callender's equation should be used [12]. It is assumed that the temperature of the metal is homogeneous.

R_T , or in this case $k \cdot R_T$ for a platinum foil, where the temperature is not homogeneous, is plotted against the temperature, measured in the middle of the platinum foil, with a thermocouple. $\frac{R_T - R_S}{R_S}$, where R_S is the resistance of the platinum foil at the same temperature as the surroundings, is plotted in the same way (fig 1). It will be noted that the results give an almost linear response. Both curves are plotted to demonstrate how R_S and the temperature coefficient influence the slopes of the curves.

The two straight lines in figure 1 are drawn between the first and last points. The deviation from the two lines is greatest at ca 500°C , but is nowhere more than 10°C .

A constant γ defining the resistance change per degree C that occurs in the centre of the platinum foil could replace the α term in equation (1) giving:

$$R_T = R_S [1 + \gamma (T - T_S)] \quad (2)$$

where the value of $\gamma \approx 0.3 \cdot \alpha$ for the apparatus used in this investigation.

R_T = the resistance of the platinum foil when the temperature is $T^{\circ}\text{C}$ in the middle.

R_S = the resistance of the platinum foil when the temperature is homogeneous in the foil and the same as the surroundings, T_S .

γ = resistance change in the foil for 1°C change of the temperature in the middle.

In order to calibrate the temperature changes in a foil without thermocouples, the resistance of the foil, at two known temperatures, is needed. One temperature is easy to measure, namely the temperature which occurs when the resistance is R_S . This temperature T_S is slightly different from that of the pyrolysis chamber (T_S is 108°C when the chamber is 115°C), one reason being that the foil is cooled by the carrier gas. The other required temperature may be determined with the aid of the temperature calibrated photodiode.

The temperature of three different platinum foils (a, b and c) were measured with thermocouples. At the same time, the light from the foils at higher temperatures was measured with a photodiode, placed under the foils ((7), fig 1b). The results are presented in figure 2, where the logarithm of the response from the photodiode is plotted against the temperature from the thermocouples. The different results obtained with the three foils can be due to error in the measurement with the photodiode or to non-reproducible spot-welds for the thermocouples, giving rise to error in the signal measured.

As the platinum foil expands when heated, the exposure of different areas to the photodiode could be responsible for the variations in the response. Experiments have been

conducted in which the position of a foil has been moved a few mm away from the photodiode, but the changes measured were so small and foil movement cannot be used to explain differences of $\pm 10^{\circ}\text{C}$. In the pyrolysis experiments the foil is actually only moved a few tenths of a millimeter. The differences in temperature measured with foils a, b and c, while the photodiode response is constant, must be explained by differences in the fastening produced in the spot-welding of the thermocouples.

The uncertainty in the temperature at the highest mean value of the calibration of the photodiode, 873°C , was estimated to be $\pm 10^{\circ}\text{C}$. Many foils, including a, b and c, were examined. High values, due to a voltage drop in the thermocouple, could be detected by changing the current direction through the foil. It was difficult to prove that very low values were due to the positioning of the contact point, in the thermocouple, too high above the foil.

The second known temperature for the two-point calibration line is measured when the photodiode has a response of 6 mV. The temperature at the middle of the platinum foil is then 873°C (see fig 2).

Figure 3 shows a two-point calibration line in which $\frac{R_T - R_S}{R_S}$ is plotted against the temperature.

Check of the pyrolysis temperature and of the reproducibility of the TRT at low temperatures by pyrolysis of polybutadiene.

Polybutadiene has been examined at different pyrolysis temperatures and times, and it is intended that these experiments will be published in detail at a later date. It was shown that the amount of polybutadiene decomposition varied with the pyrolysis temperature. For any selected temperature the amount of monomer produced was proportional to that temperature. No further reaction producing the monomer took place, with the substance left

on the foil, until the temperature was increased. For temperatures between ca 450 and 550°C, it was shown that the rate of decomposition to the monomer appeared to be first-order. The pyrolysis products consisted primarily of butadiene, monomer, peak no 1, and vinylcyclohexene, dimer, peak no 7 [7, fig 9]. If the pyrolysis time is constant, a correlation may occur between pyrolysis products and pyrolysis temperatures.

The first current pulse will of course influence the results if it is too high or too low. For this reason the TRT should be checked. The TRT is easy to control at high temperatures where the photodiode can be used.

It has been shown experimentally that if the total pyrolysis time (two seconds in most experiments reported here) is divided into a number of pyrolyses of shorter pyrolysis time, approximately the same results are obtained if the TRT is short enough.

For this work, a two second pyrolysis has been divided into ten 208 msec pyrolyses. The first current pulse is 8 msec, and if the correct value of the first pulse is chosen, the TRT, during which no pyrolysis reaction occurs, should be 8 msec as well [7]. The integrator counts from the butadiene peak (no 1) are summed for the ten pyrolyses, Σ_1 .

If Σ_1 differs from the value obtained for a 2 second pyrolysis, the temperature time profile of the first 200 msec, after the TRT, will differ from that for the remaining 1.8 seconds.

In figure 4, curve 1, 0, the integrator counts from the butadiene peak (no 1), resulting from the 2 second pyrolysis of polybutadiene, is plotted against the pyrolysis temperature. The temperatures have been estimated from figure 3. At these low temperatures, the substance is not totally pyrolyzed.

In figure 4, curve 2, O , the monomer to dimer ratio, peak no 1 and peak no 7, has been plotted. If the response of the gas chromatograph detector changes during experiments this curve can be used for recalibration. Changes of a few degrees centigrade in pyrolysis temperature will cause a much greater change in the decomposition products than normal variation in the detector response.

In figure 4, curve 3, $\square$, Σ_1 has been plotted. A difference in the results can be seen between curves 1 and 3. This means that the formation of monomer in the sample is less during the first 200 msec than during the remaining pyrolysis time. By careful adjustment of the first pulse a closer agreement between the curves could be obtained. This is however not necessary in order to check reproducible TRT:s between different foils.

When the pyrolysis temperature is to be checked the same amount of polybutadiene is pyrolyzed using similar conditions to those used to construct calibration curve no 1 in figure 4. The integrator counts from the butadiene peak are compared with curve no 1, and the temperature, T_1 , is read on the x-axis. When the TRT is to be checked the same amount of polybutadiene is pyrolyzed under similar conditions to those used to construct calibration curve no 3 in figure 4. The result of Σ_1 is compared to the curve and the T_{Σ_1} is read on the x-axis. T_{Σ_1} is not a temperature, but may be regarded as a temperature profile for the first 208 msec.

Temperature calibration of a platinum foil for different surrounding temperatures and a check of the pyrolysis temperature under these changing conditions.

If the temperature of the chamber is changed, the temperature of the platinum foil is likewise changed, as is the resistance, R_s . The slope of the calibration curve in which $\frac{R_T - R_s}{R_s}$ is plotted vs T should not change, provided

γ is not dependent on T_s ; however, the slope of $k \cdot R_T$ vs T should change.

The temperature of the pyrolysis chamber was varied between 100 and 130°C. The foil was calibrated in the same fashion as before, and the results are shown in figures 5 and 6.

The temperature of the photodiode did not increase when the temperature of the chamber was increased.

Figure 5 shows that the slope, γ , varies with a change in T_s such that γ varies inversely with a change in the temperature of the surroundings, which in turn, depends on differences in the temperature at the ends of the foil.

In figure 6, the slope, $k \cdot R_s \cdot \gamma$, does not change as much as the slope in figure 5, since the increase in γ is partially compensated by the decrease in R_s when T_s is decreased. If a constant value for $k \cdot R_T$ is chosen and the surrounding temperature is changed approximately 30°C, the change in pyrolysis temperature is about 15°C.

To check that a desired pyrolysis temperature could be obtained with a two point calibration curve even if the temperature of the pyrolysis chamber was changed, 7.4 μg of polybutadiene were pyrolyzed at chamber temperatures of 100, 115 and 130°C. At each temperature the current pulses were adjusted to give a desired pyrolysis temperature, $T_{\text{cal}}^{\circ}\text{C}$, as read from the two point calibration lines. (For results see table I.) The integrator counts from peak no 1 were used to estimate the temperature $T_1^{\circ}\text{C}$ from figure 4, curve no 1. To check the temperature profile of the first 200 msec, Σ_1 was estimated and the value T_{Σ_1} was determined from figure 4, curve no 3. The results show that the desired temperature could be reproduced even if the temperature of the pyrolysis chamber was changed.

Reproducibility of pyrolysis temperature and TRT for different platinum foils.

Temperature calibration lines were made for five different foils (fig 7). It was shown that γ differed for different foils; this dependency probably results from the fastening of the foils and different dimensions of the foils, which will change the temperature gradient within the foil.

Experiments were carried out to choose a pyrolysis temperature of approximately 440°C for each foil. The current pulses were adjusted to give the value for $\frac{R_T - R_S}{R_S}$, corresponding to about 440°C on the calibration curve for each foil (fig 7 (the lines on the right)) and the proper TRT. Polybutadiene was pyrolyzed on each foil at this temperature, $T_{\text{cal}}^{\circ}\text{C}$, to check the pyrolysis temperature by $T_1^{\circ}\text{C}$ and the TRT by T_{Σ_1} . The results are given in table II. It may be seen from table II that both the temperature and the TRT could be reproduced even if the foil was changed.

The relative errors in determining the value of $\frac{R_T - R_S}{R_S}$, including errors of the voltmeters, was estimated to be $\pm 2^{\circ}\text{C}$. The reproducibility of the pyrolysis results is about $\pm 1\%$, which, in the temperature range of the calibration curve, means less than $\pm 1^{\circ}\text{C}$ when $T_1^{\circ}\text{C}$ is estimated.

The results in table II show that a temperature approximately 5°C too high compared to the set temperature, $T_{\text{cal}}^{\circ}\text{C}$, was obtained with foil no 3. The temperature could be adjusted more precisely if desired. In figure 8, foil no 3 is adjusted by the two current pulses to the desired temperature. Point no 1 in figure 8, curve 1 and 2, shows the first temperature obtained; they are too far above 442°C . Besides, the high temperature the TRT was too low. The no 1 points do not fall under each other. Point no 1 on curve 3 is too low compared to point no 1 on curve 1.

This means that the first pulse is too low. On increasing the first pulse, points no 2 of the three curves fall under one another. On lowering the second pulse, the temperature decreases about 4 degrees but the TRT is too high (point no 3, curve 2). Upon lowering the first current pulse this will be adjusted (points no 4) and the temperature was adjusted to 441°C and a similar TRT as for the calibration curve was obtained.

In this way, the pyrolysis temperature and the TRT can be adjusted with the two current pulses and both can be checked by the controlled pyrolysis of polybutadiene.

Substance placed on the upper side of the platinum foil or on the lower side.

Table III shows how the pyrolysis results differed if the substance was placed on the upper side or on the lower side of a platinum foil in the absence of a thermocouple. The difference in results corresponds to a temperature difference of less than 1°C (curve 1, fig 4).

Pyrolysis of different batches of Cariflex 1220.

Five different batches of polybutadiene were pyrolyzed twice. The results are given in table IV. The difference between batch-means was examined by means of an analysis of variance (one-way classification). No significant difference at the 0.05 level was detected ($p=0.052$).

This means that when using cis-1.4-polybutadiene (Cariflex 1220) for checking the pyrolysis temperature, different batches of the sample will not give greater differences in the pyrolysis results than the differences which are obtained within the same batch. In this case results from the highest and lowest values in table IV corresponds to a variation of temperature of 3°C (curve 1, fig 4).

Conclusions:

From the estimated resistance of a platinum foil and the temperature received from a calibrated photodiode a two

point calibration line could be made. This calibration line could be used to adjust the pyrolysis temperature within the whole temperature interval.

To check the temperature received from a two point calibration line cis-1.4-polybutadiene (Cariflex 1220) could be used. The reproducibility of the temperature measurements with the resistance is not as good as that obtained by the pyrolysis of polybutadiene.

With pulse pyrolysis of polybutadiene the temperature profile at the first 200 msec could be checked, at low temperatures where the photodiode has no response.

Acknowledgement:

The author wishes to thank Dr Lars Haraldson for valuable discussions concerning this work and Dr Robert Carter for revision of the English text.

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- R_T The resistance of the platinum foil when the temperature is $T^{\circ}\text{C}$ in the middle.
- $k \cdot R_T$ A value proportional to the resistance of the platinum foil when the temperature is $T^{\circ}\text{C}$ in the middle. This value is the voltage drop across the platinum foil divided by the voltage drop across constant resistance in series with the platinum foil. Thus $\frac{1}{k}$ is the value of the constant resistance.
- R_s The resistance of a platinum foil when the temperature is homogeneous in the foil and the same as the surroundings, T_s .
- γ Resistance change in the foil for 1°C change of the temperature in the middle.
- T_s The temperature of the surroundings.
- T The temperature in the middle of a platinum foil.
- Σ_1 The sum of the integrator counts from peak no 1, obtained by pyrolyzing polybutadiene ten times for 208 msec.
- T_1 The temperature obtained from curve no 1 in figure 4 when the integrator counts from peak no 1 is used for temperature determination.
- T_{Σ_1} This value is obtained when Σ_1 is compared with curve no 3 in figure 4 and T_{Σ_1} is read on the x-axis.
- T_{cal} The temperature determined by a two point calibration line.

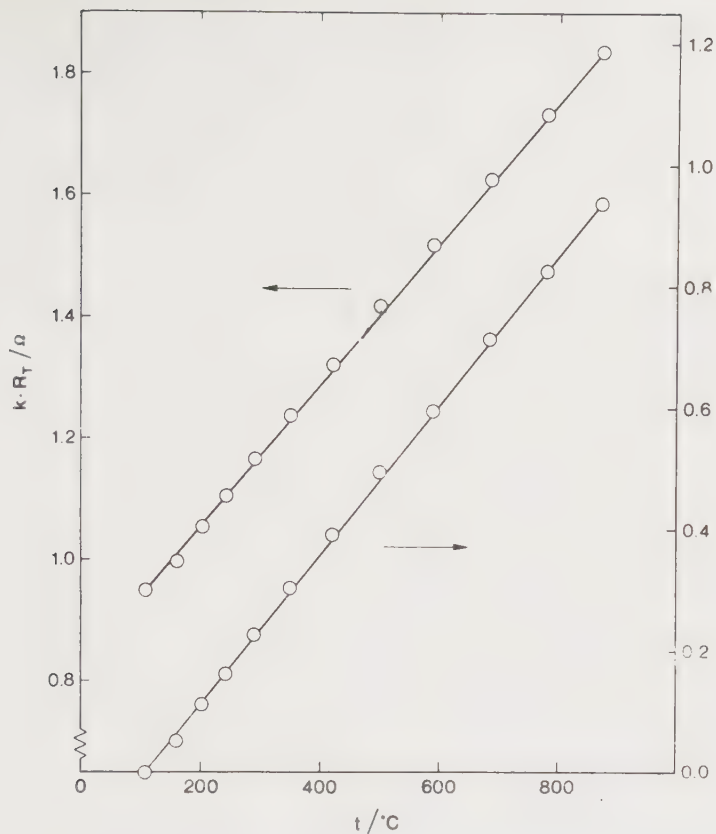


Figure 1: $k \cdot R_T$ and $\frac{R_T - R_S}{R_S}$ plotted against the temperature measured with thermocouple.

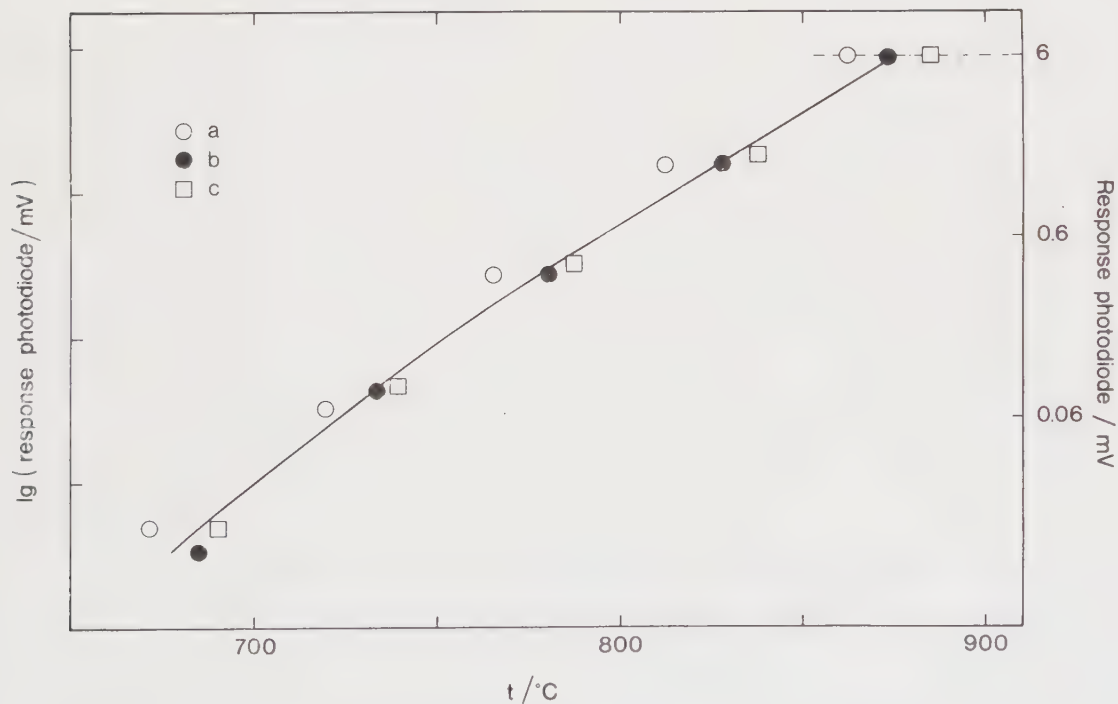


Figure 2: Log (photodiode response) plotted against the pyrolysis temperature measured with a thermocouple for each of the three different foils (a, b and c).

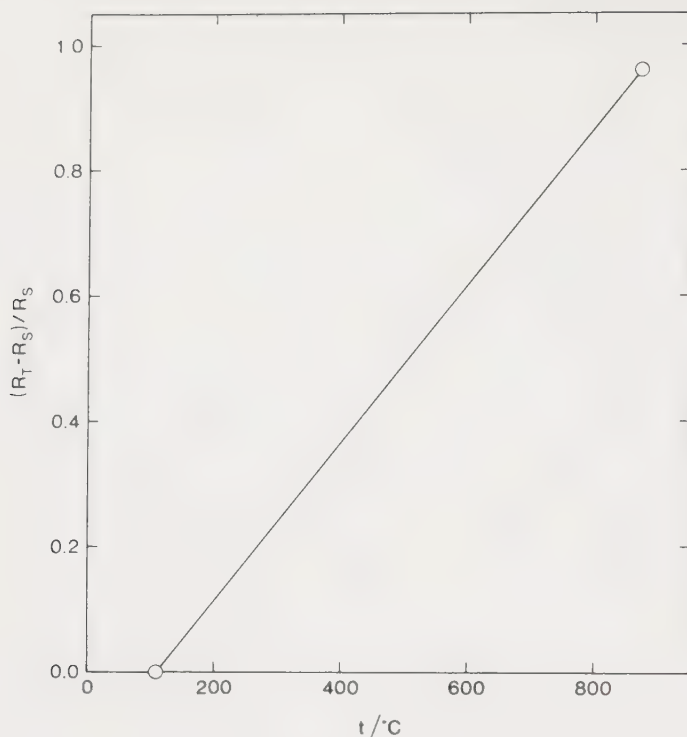


Figure 3: A two point temperature calibration line for the foil used while making the pyrolysis calibration curve.

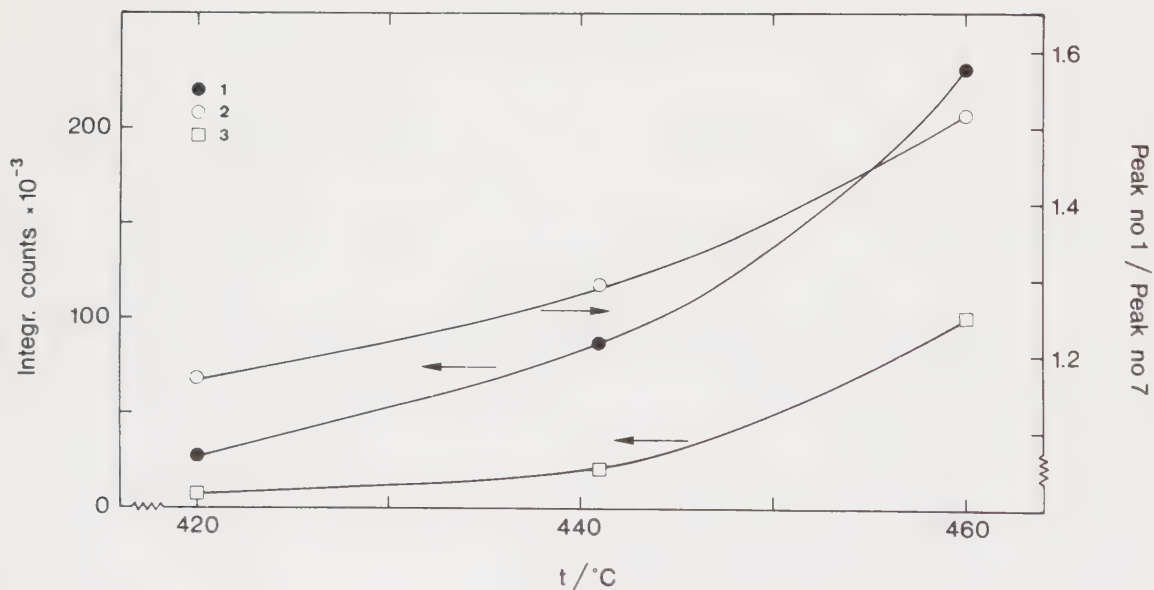


Figure 4: A temperature calibration curve made by pyrolyzing 7.4 μg of polybutadiene for 2 seconds at three different temperatures.

Curve no 1: Integrator counts of peak no 1.

Curve no 2: Integrator counts of the monomer/dimer ratio, $\frac{\text{peak no 1}}{\text{peak no 7}}$.

Curve no 3: Integrator counts of peak no 1 summed for ten 208 msec pyrolyses of the same sample, Σ_1 , plotted against the temperature obtained after 2 seconds.

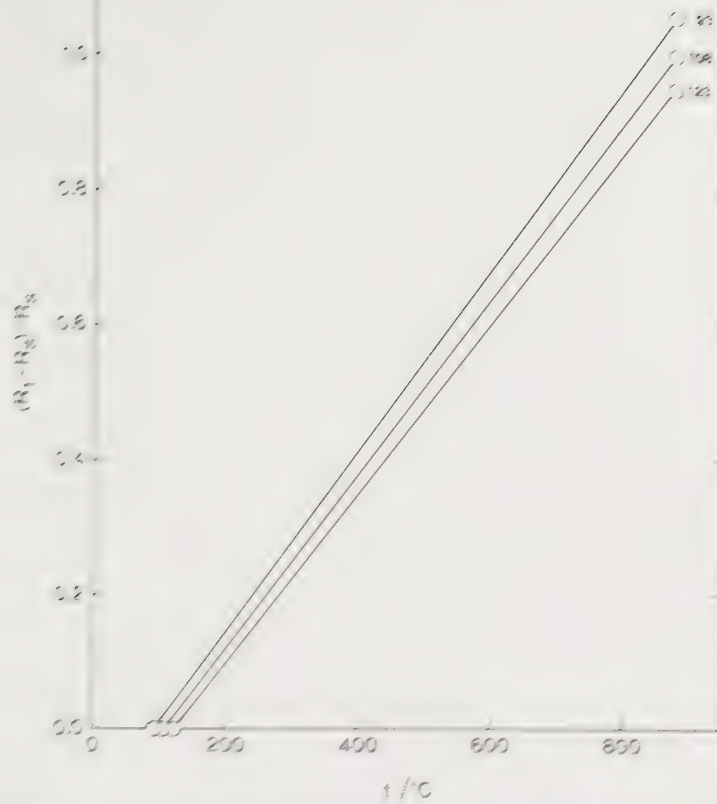


Figure 5: Two point temperature calibration lines for the same foil at three different temperatures of the surroundings (93, 108 and 123°C). $\frac{R_T - R_S}{R_S}$ against the temperature.

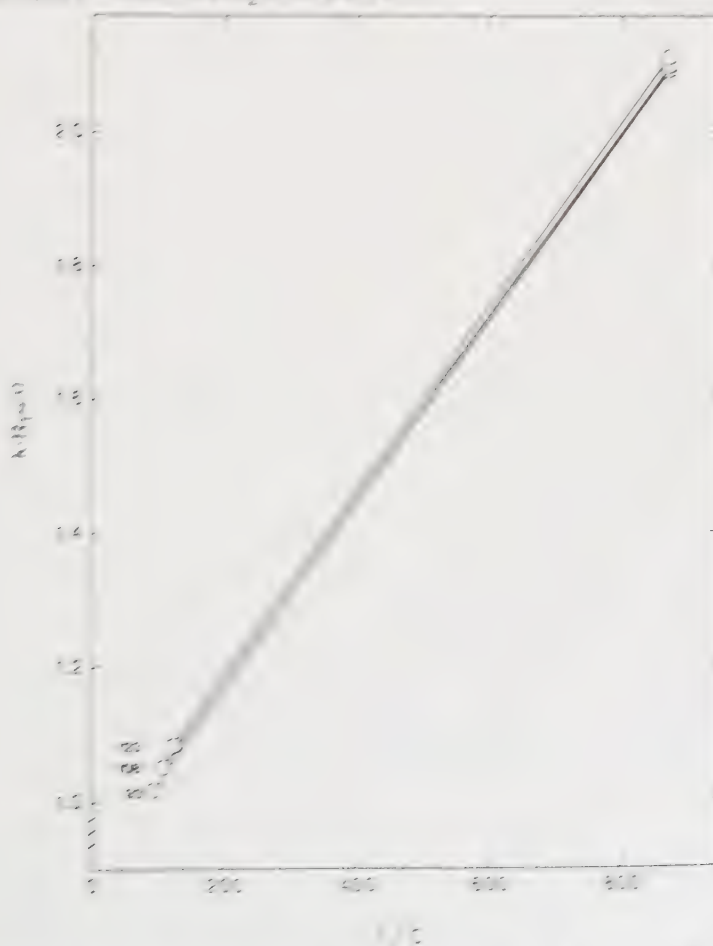


Figure 6: Two point calibration lines for three different temperatures of the surroundings (93, 108 and 123°C). $k \cdot R_T$ against the temperature.

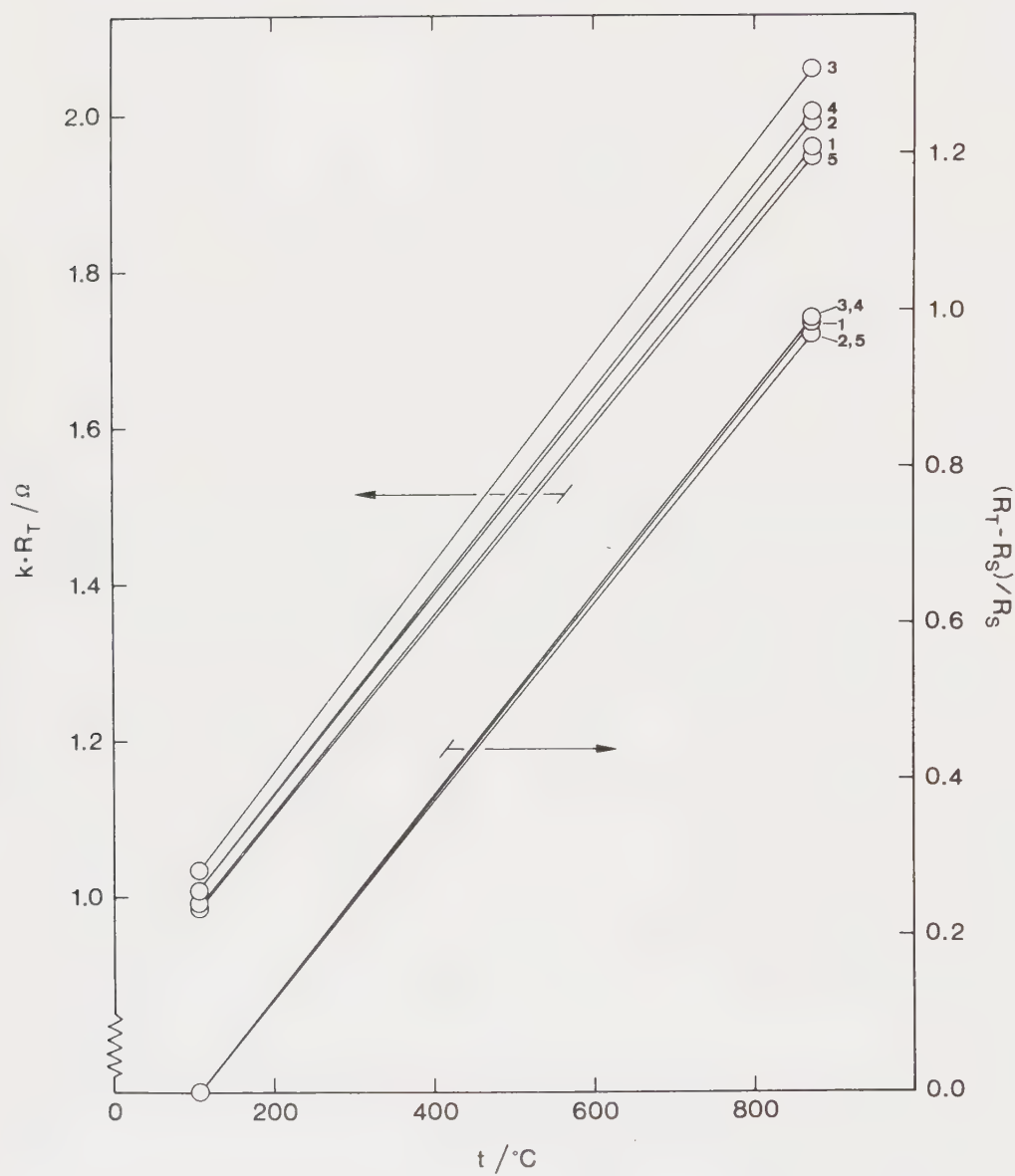


Figure 7: Two point temperature calibration lines for five different foils. Both $k \cdot R_T$ and $\frac{R_T - R_S}{R_S}$ plotted against the temperature.

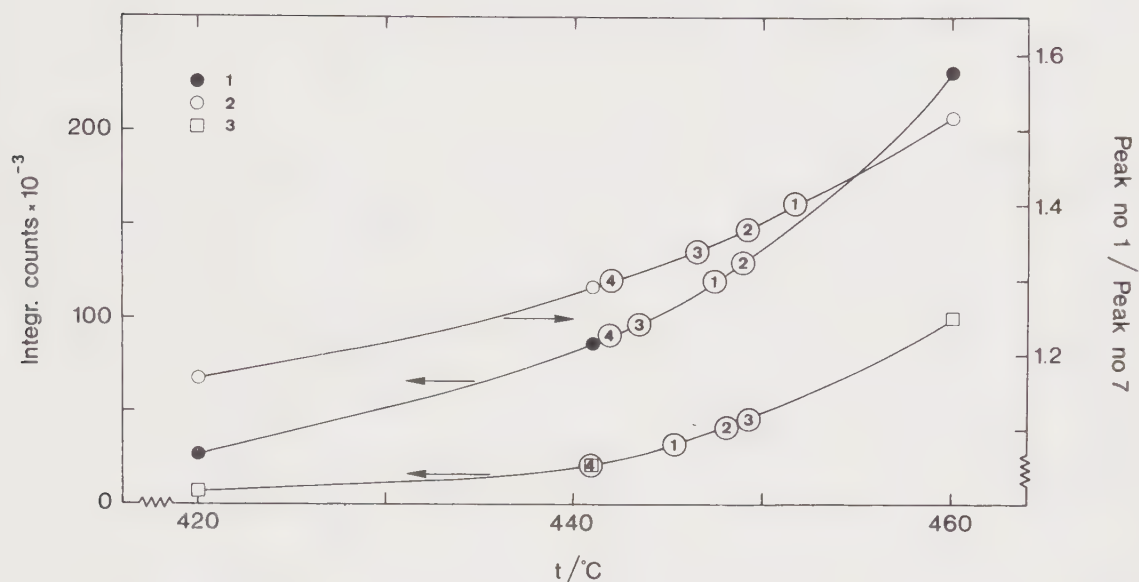


Figure 8: The influence of a change in the two current pulses; checked by pyrolyzing polybutadiene.

Point no	1	2	3	4
First current pulse	494	499	499	490
potentiometer value				
Second current pulse	176	176	175	175
potentiometer value				

Increasing value of the potentiometers will increase the amplitude of the current pulse.

Table I: The pyrolysis chamber temperature is varied between 100 and 130°C; the pyrolysis temperatures were adjusted with the aid of the calibration lines in figure 5 and determined by pyrolyzing polybutadiene (7.4 µg).

T_s °C	T_{cal} °C	Peak no 1 integr counts	T_1 °C	Σ_1 integr counts	T_{Σ_1}
93	447	129604	449	41829	448
107	445	106095	445	31403	444
123	445	104856	445	27414	443

Table II: With the aid of two point calibration lines five different platinum foils are set to the temperature, T_{cal} °C, approximately 440°C. The temperature on each foil was checked by pyrolyzing polybutadiene (7.4 µg).

Foil no	T_{cal} °C	Peak no 1 integr counts	T_1 °C	Σ_1 integr counts	T_{Σ_1}
1	440	119636	447	47482	449
2	441	108046	445	46163	449
3	442	120653	447	33722	445
4	442	103827	445	40311	447
5	440	123057	448	43035	448

Table III: 7.4 μg Polybutadiene pyrolyzed for 2 seconds at 460°C on the upper side and on the lower side of the same platinum foil.
Peak no 1 = butadiene.

Pyrolysis no	Peak no 1 integr counts
Over	
1	194573
2	198585
Under	
1	203517
2	199959

Table IV: 7.4 μg Polybutadiene from five different batches of Cariflex 1220 pyrolyzed at 445°C for 2 seconds. The integrator counts from peak no 1 is tabulated.

Batch no	I	II	III	IV	V
Pyrolysis no					
1	110772	106757	104174	110010	101143
2	106817	103075	103276	106574	96344

DECOMPOSITION STUDIES OF CIS-1.4-POLYBUTADIENE BY PYROLYSIS GAS CHROMATOGRAPHY.

Part I: Pyrolysis at low temperatures with short temperature rise times.

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Summary:

Cis-1.4-polybutadiene has been pyrolyzed in a temperature interval between 450°C and 530°C where the temperature rise time (TRT) of the pyrolyzer used can be regarded as short. The rate of decomposition to the monomer appeared to be a first-order reaction. The activation energy was determined to be 37.5 kcal/mole (157 kJ/mole). A technique called pulse pyrolysis was introduced, which was found to be less time consuming than the ordinary method, and errors from sample handling were decreased.

Introduction:

The pyrolysis technique in combination with gas chromatography is a useful tool for qualitative analysis of polymers. Attempts have also been made [1,2,3] to use this technique for kinetic studies of polymer decomposition, but this application has been very limited, probably due to difficulties in obtaining the necessary control of pyrolysis temperature and temperature rise time (TRT).

Using a pyrolysis unit Madorsky [4] studied the thermal degradation of organic polymers in vacuum and analysed

one of the fractions obtained with mass spectrometry. Most decomposition studies so far have used thermal gravimetric analysis (TGA) [5,6].

It is generally assumed that for kinetic studies a pyrolyzer, which works under ideal conditions, is required. This means that the sample is decomposed at a constant temperature and no secondary effects take place. In practice, this means that the temperature rise time (TRT) must be short, and that the pyrolysis temperature must be kept constant. Furthermore, there should be no temperature gradient where the sample is placed in the pyrolyzer, there should be a short cooling time for the pyrolyzer and it should be capable of handling a small amount of sample.

To pyrolyze with a short TRT means that the pyrolysis temperature used must be chosen to suit both the sample which is to be pyrolyzed and the TRT of the pyrolyzer. The TRT for most pyrolyzers will probably be short for low pyrolysis temperatures. It is important that the TRT should only be a small per cent of the total pyrolysis time. For pyrolysis at high temperatures, the requirement for very fast temperature rises is pronounced.

In most papers on pyrolysis gas chromatography, excessively high temperatures are used, which means that most of the sample decomposes during the temperature rise where the conditions are not known [7].

The aim of this paper is to show that it is possible to pyrolyze a substance at nearly ideal TRT in a limited temperature interval. This interval is limited by the TRT of the pyrolyzer at the highest pyrolysis temperature and at the lowest temperature by the pyrolysis time.

The kinetics of the decomposition of cis-1.4-polybutadiene has been studied by pyrolysis in the temperature range 450-575°C. A new technique called pulse pyrolysis

is introduced and its potential as a pyrolytic technique is compared to currently accepted pyrolysis methods.

Experimental:

Apparatus and temperature calibration.

The apparatus and temperature calibration method used has been presented earlier in detail [8,9]. The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide. It is heated by two current pulses. The first is 8 msec for all pyrolysis temperatures. A photodiode is placed under the foil to measure the temperature of the foil at high temperatures. The pyrolyzer is linked to the column of a gas chromatograph. The stationary phase of the column is 15% Apiezon L on Chromosorb DMCS 80-130 mesh and the temperature of the column is 150°C. The temperature of the pyrolysis chamber is 115°C and the carrier gas flow rate is 20 ml/min. A flame ionisation detector is used. The peak area of the pyrolysis products is measured by an electronic integrator. The temperature of the pyrolyzer is determined by measuring the resistance of the platinum foil and the response of the temperature-calibrated photodiode.

Sample preparation.

14.7 mg of 96.5% cis-1.4-polybutadiene was dissolved in 2 ml of toluene. 1 µl of the solution was placed on the platinum foil by means of a 1 µl Hamilton syringe. The toluene was evaporated before pyrolyzing the sample.

Ordinary pyrolysis.

The usual way of pyrolyzing a sample involves pyrolysis at a known temperature for a certain time. Between each pyrolysis the pyrolyzer is cleaned. In this work the platinum foil was heated in a Bunsen flame. After cleaning, the sample was positioned on the platinum foil and the pyrolyzer was placed in the pyrolysis chamber. Before the sample could be pyrolyzed, a small residue of solvent must be removed from the column and the carrier gas pressure must be stabilized. A total of about half an hour

is required between each ordinary pyrolysis reported in this paper.

Pulse pyrolysis.

Pulse pyrolysis is simply the repetition of a single pyrolysis on the same sample under the same conditions. The pyrolyzer is prepared as for the ordinary pyrolysis, but after the initial pyrolysis, any sample left on the pyrolyzer, is repeatedly pyrolyzed using the same conditions. The number of repeated pyrolyses depends on the time to decompose all of the substance or when no more pyrolysis products are produced. Each repeated pulse pyrolysis reported in this paper takes about five minutes.

Results and discussion:

Ordinary pyrolysis.

7.4 μ g of cis-1.4-polybutadiene was pyrolyzed for different times and temperatures. The integrator counts of the first peak, which for the most part consists of butadiene [10], is plotted against pyrolysis time at different temperatures in figure 1.

Two seconds at temperatures of 450 and 470°C, does not allow complete decomposition and further pyrolyses, at both temperatures for longer times were carried out to estimate the integrator counts of peak no 1 when decomposition had been completed. After about 10 and 5 seconds, respectively, no further decomposition was observed. It was shown that the amount of butadiene decomposed was higher at 470°C than at 450°C.

At 450°C the same amount of sample was pyrolyzed 5 times for 2 seconds and the results are presented in figure 2. It can be seen that the amount of product formed decreases with each succeeding pyrolysis. After the fifth pyrolysis, a sixth pyrolysis was carried out at 1000°C. This time much larger quantities of products were obtained. This shows that there is undecomposed sample left on the foil. In fact only about 10% of the total substance had been

pyrolyzed at 450°C.

For temperatures of 490, 510 and 532°C, figure 1 shows that the decomposition had ceased after 2 seconds or less. The amount of monomer formed increases with increasing temperature.

At the two highest temperatures, 552 and 575°C, the monomer yield also increases with temperature (fig 1). For these two temperatures the plots show a decrease in monomer yield after a certain pyrolysis time. At 575°C the amount of monomer formed increases with time, and after a small decrease it increases again, and at 300 msec the amount of monomer decreases. This rise and fall of the amount of monomer must depend on a combination of an increase in the pyrolysis temperature and secondary effects. The following explanation for the appearance of the curve may be offered. After about the first 100 msec, the decomposition of the monomer is finished and then secondary effects may be observed until an increase in the temperature takes place. After 300 msec, when the temperature is at its maximum, further secondary effects may be seen.

In figure 3, the pyrolysis temperature is plotted against time. The temperature has been measured with the photodiode. The temperature-time profile in the middle of the foil where the sample is placed shows that there is a temperature variation in the platinum foil during the first 300-400 msec. This variation is not more than $\pm 10^\circ\text{C}$.

A series of experiments was carried out with a platinum pyrolyzer to prove that secondary effects are present when pyrolysis occurs at low temperature. Butadiene and vinylcyclohexene were injected in the carrier gas in such a way that they passed over the platinum foil in the pyrolysis chamber and the peak areas were measured. Again the same amount of substance was injected and at the same time the pyrolyzer was heated to about 500°C for 2 seconds. This time the peak areas decreased.

It is noticeable that the amount of peak no 1, as well as that of the other peaks, increases with increasing temperature. One explanation for this observation is that higher oligomers will be produced at low temperatures, but they are not detected as they do not pass through the column. At higher temperatures the high-boiling products will be decomposed to give more low-boiling products. In figure 2 it is shown, however, that most of the sample remains on the foil.

During the pyrolysis of polybutadiene, in vacuum, with temperatures up to 475°C , Madorsky [4] found that at higher pyrolysis temperatures the monomer fraction falls off in yield. He explained this by the occurrence of cross-linking and carbonization.

In a later paper it will be shown that the amount of decomposition product will be nearly independent of how the substance is heated. It is only the maximum temperature that influences the degree of decomposition.

If a sample is homogeneous the whole sample should be totally pyrolyzed after a certain time at a constant temperature. The cis-1.4-polybutadiene used in these experiments was shown to be only partly decomposed at each temperature even when the pyrolysis time was increased. This suggests that the sample was not homogeneous. However, if the sample is chemically pure the only thing that could be nonhomogeneous is the molecular weight, i.e. the sample consists of pure polybutadiene fractions of varying molecular weights. One explanation for the observed temperature dependence of the decomposition could be that the initiation of the decomposition becomes increasingly difficult the lower the molecular weight of the fraction. This may be verified if pyrolysis experiments are carried out using butadiene of different molecular sizes.

Pulse pyrolysis.

The same substance was pyrolyzed for several 208 msec intervals until no further decomposition products were produced. The same current pulses, as for the ordinary pyrolysis were used. The decomposition products from a 2 second ordinary pyrolysis are the same as the products formed by pyrolyzing the same amount of sample ten times for 208 msec, provided the temperature of the 200 msec after the TRT is the same as the temperature of the 2 second pyrolysis. The decomposition results at the four lowest temperatures were nearly the same (compare fig 1 and 4). The difference in results corresponds to a few degrees centigrade, which means that the mean temperature of the 200 msec after the TRT was almost equal to the temperature of a 2 sec pyrolysis.

At the three highest temperatures, the reaction rate was so fast that 108 msec or shorter pulses had to be used in order to obtain more than one value before the decomposition was completed (see fig 3). This leads to a lower mean temperature of the pulses compared to a pyrolysis for a longer time with the same current pulses.

Reaction order of the decomposition to the monomer.

To estimate the reaction order of the decomposition to butadiene, the ratio C/C_t must be known. C is the amount of monomer formed at each time and C_t the total amount of monomer formed when the decomposition is finished. For a first-order reaction $-\ln (1 - \frac{C}{C_t}) = k \cdot t$.

k is the decomposition rate and t the pyrolysis time. If cis-1.4-polybutadiene is pyrolyzed at different temperatures, C_t will differ (fig 1 and 4).

In figure 5, $-\ln (1 - \frac{C}{C_t})$ is plotted against time for both an ordinary pyrolysis and a pulse pyrolysis at 490°C . For the pulse pyrolysis it can be clearly seen that monomer formation is a first-order reaction. The

scatter of the points obtained with ordinary pyrolysis is much larger and the linear relationship is more difficult to detect. Thus for kinetic studies it is more suitable to pulse pyrolyze the sample.

In figure 6, $-\ln(1 - \frac{C}{C_t})$ is plotted against time for the pulse pyrolysis in the temperature interval 450-575°C. Monomer formation seems to be a first-order reaction in the entire temperature interval. The reaction half life, $t_{1/2}$, was calculated (see the table).

The $t_{1/2}$ was used for calculating $\ln k$ which is plotted against $\frac{1}{T}$ to make an Arrhenius plot (fig 7). From these results the activation energy may be estimated to be 37.5 kcal/mole (157 kJ/mole) in the temperature interval 450-530°C.

In the table the reaction half lives and the minimum pyrolysis time are tabulated for various pyrolysis temperatures. The minimum pyrolysis time is defined as the time required for 99.5% reaction to take place, i.e. $8 \cdot t_{1/2}$. This minimum pyrolysis time can give an indication of the maximum temperature which can be used for pyrolysis at a short TRT.

The minimum temperature is limited by the pyrolysis time. For ordinary pyrolysis the pulse time may last about 10 seconds. The longer the pyrolysis time the poorer the resolution of the decomposition products on the gas chromatograph. The maximum temperature is limited by the TRT of the pyrolyzer used. In this case, when the pyrolysis temperature is nearly linearly increased during eight milliseconds, and the decomposition follows a first-order reaction, about one per cent of the decomposition will occur when the total pyrolysis time is 108 msec.

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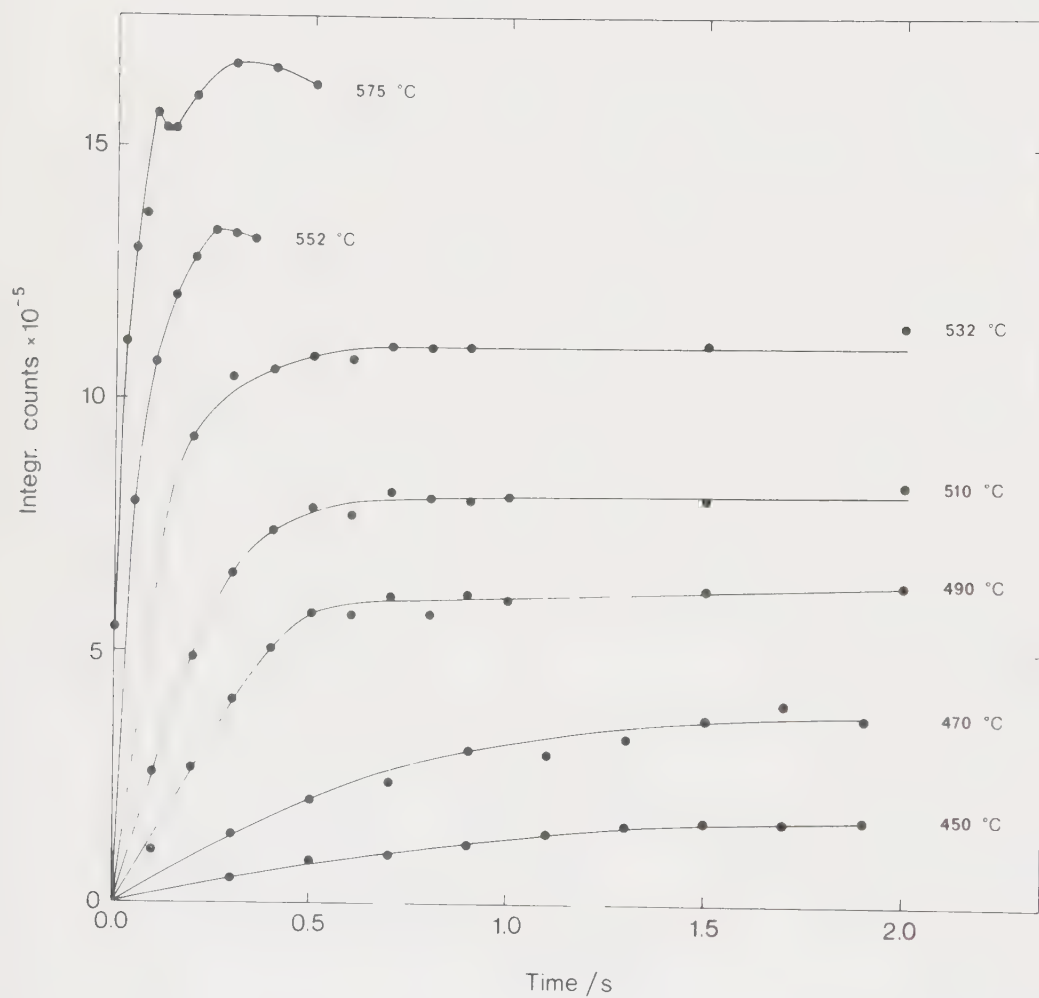


Figure 1: 7.4 μg of cis-1,4-polybutadiene pyrolyzed for different times and at different temperatures. The integrator counts of peak no 1 from the pyrograms are plotted against time.



Figure 2: The same sample of 7.4 μg of cis-1.4-polybutadiene, pyrolyzed five times for 2 seconds at 450°C and once at 1000°C.

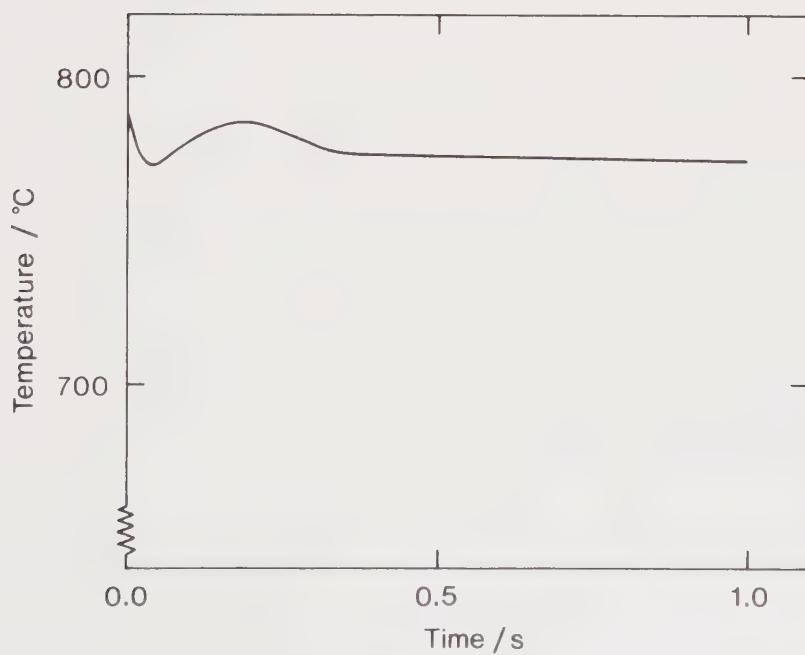


Figure 3: A temperature-time profile in the middle of a platinum foil measured with a photodiode.

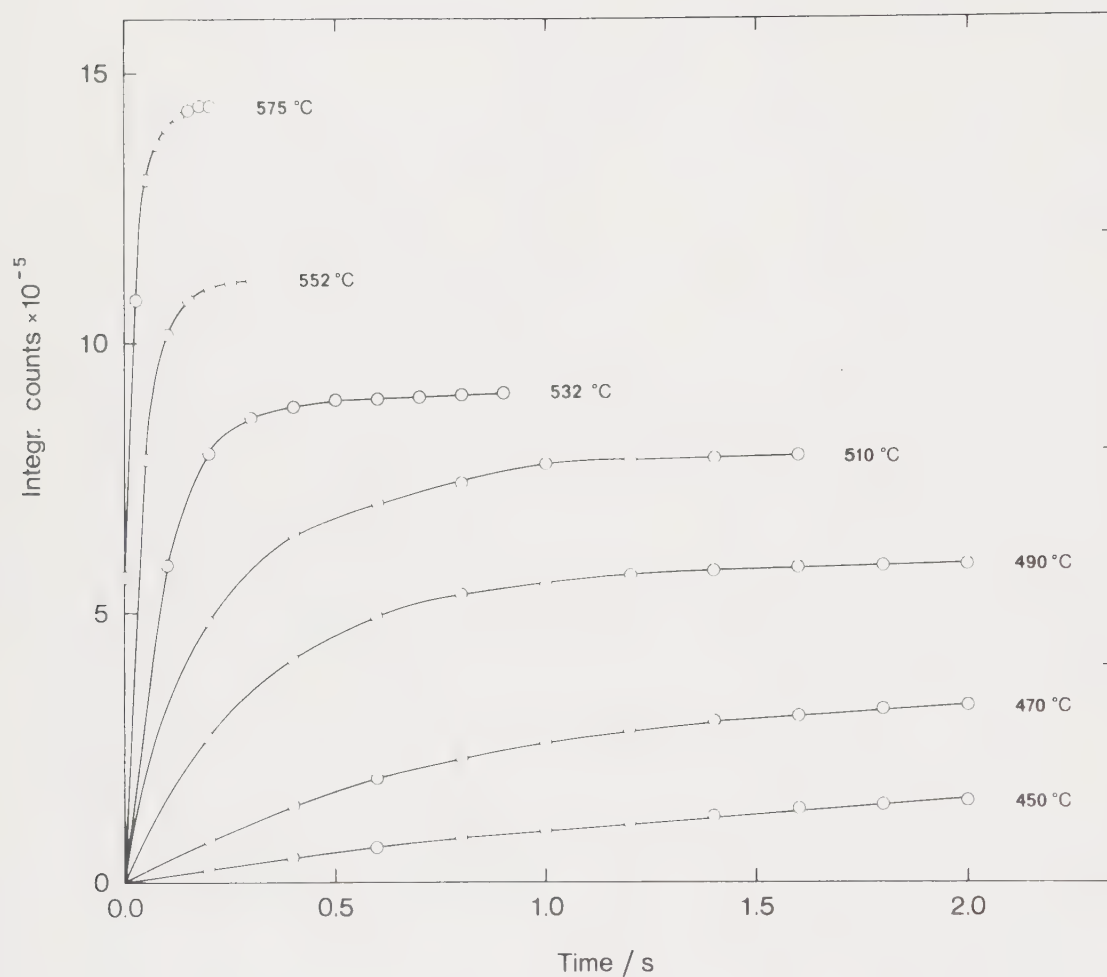


Figure 4: 7.4 μg of cis-1,4-polybutadiene pulse pyrolyzed at different temperatures. The integrator counts from peak no 1 are plotted against time. For each pulse the integrator counts and the time are summed separately.

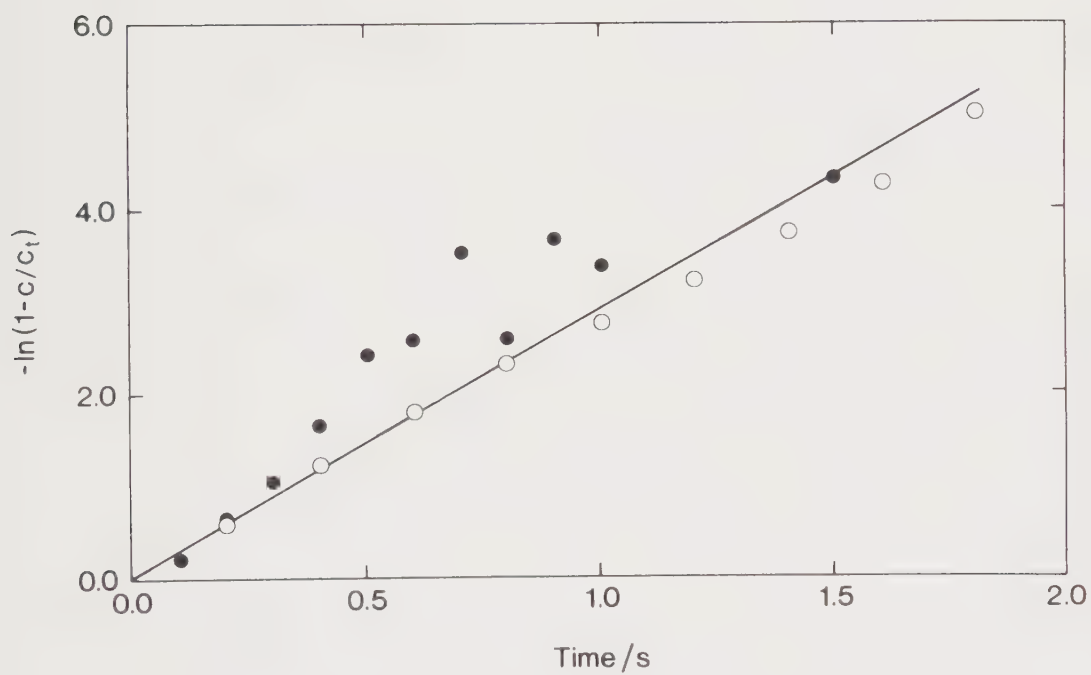


Figure 5: Plot of $-\ln \left(1 - \frac{c}{c_t} \right)$ vs time for an ordinary pyrolysis, ●, and one pulse pyrolysis, ○, at 490°C.

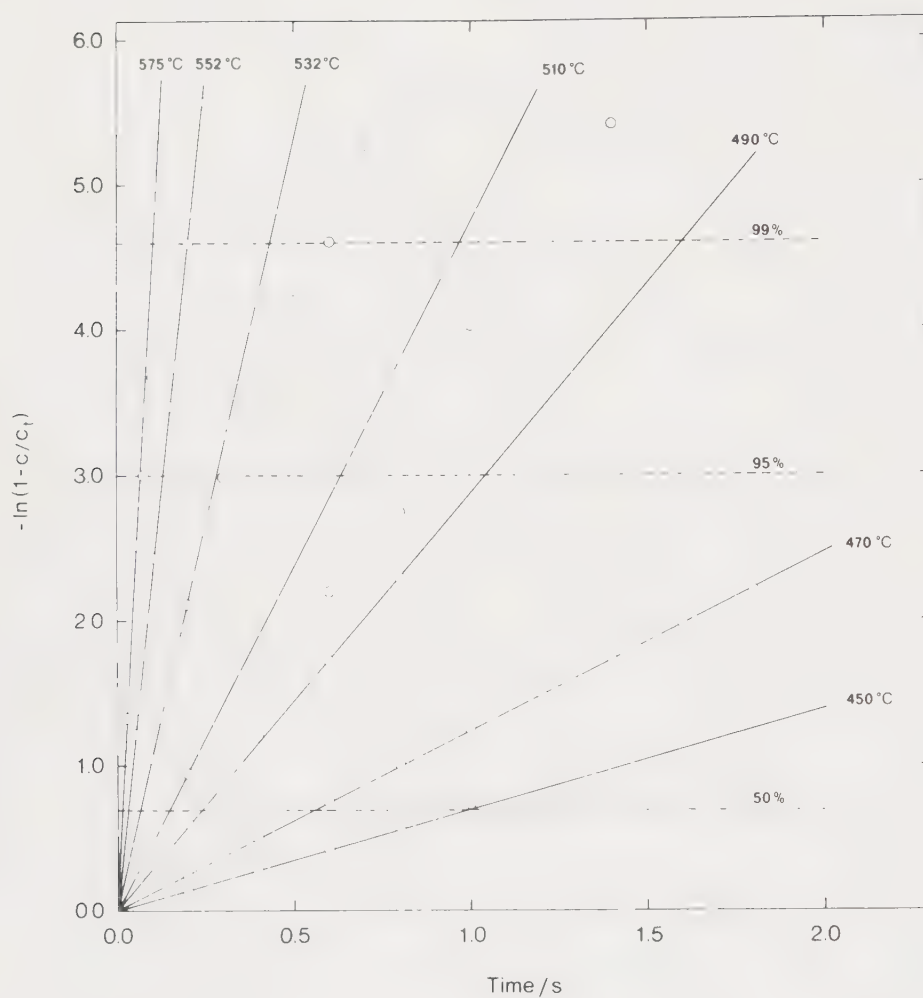


Figure 6: Plot of $-\ln(1 - \frac{C}{C_t})$ vs time for pulse pyrolysis at different temperatures.

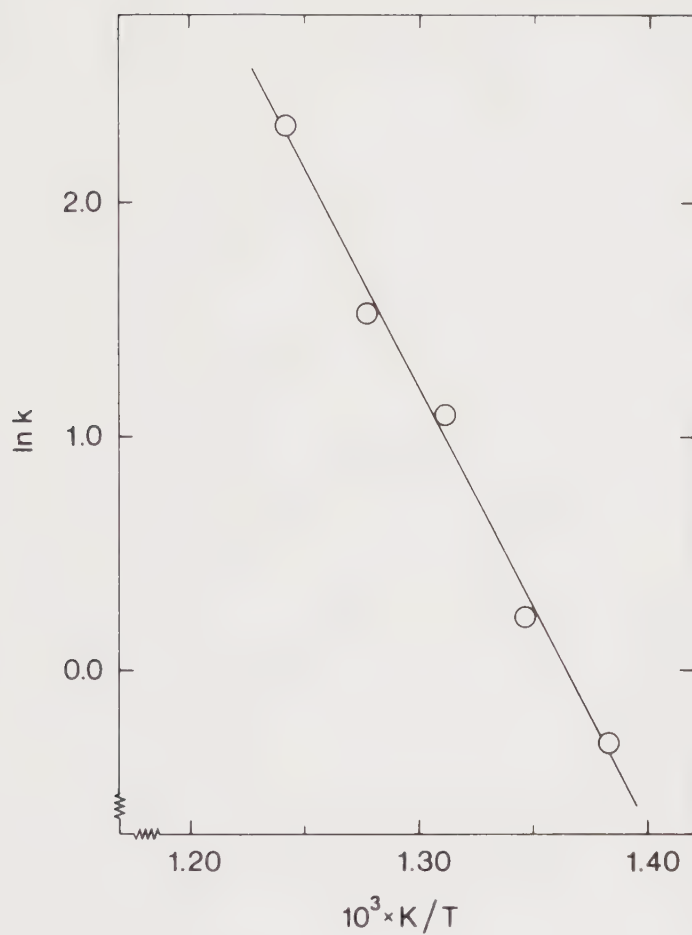


Figure 7: Arrhenius plot of the rate of the degradation of cis-1,4-polybutadiene for pulse pyrolysis at temperatures between 450 and 532°C.

Table: Pyrolysis temperatures, pulse times, half lives, minimum pyrolysis times tabulated for the pulse pyrolysis of 7.4 μg of cis-1.4-polybutadiene. Minimum pyrolysis time = $8 \cdot t_{1/2}$.

Pyrolysis temp $^{\circ}\text{C}$	Pulse time sec	$t_{1/2}$ sec	Minimum pyrolysis time, sec
450	0.208	0.95	7.60
470	0.208	0.55	4.40
490	0.208	0.23	1.84
510	0.208	0.15	1.20
532	0.108	0.067	0.54
552	0.058	0.030	0.24
575	0.033	0.015	0.12

DECOMPOSITION STUDIES OF CIS-1.4-POLYBUTADIENE BY PYROLYSIS GAS CHROMATOGRAPHY.

Part II: Pyrolysis to different end-temperatures, temperature rise times, amounts and areas.

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Summary:

Cis-1.4-polybutadiene has been pyrolyzed to different end-temperatures, temperature rise times (TRT), different amounts and sample areas. It was noticed that the amount of decomposition products increased with an increasing pyrolysis end-temperature until a temperature of 1000°C was reached. After 1000°C the total product yield decreased probably due to the on-set of carbonization (a possible secondary effect). The results of the pyrolyses to different end-temperatures were nearly independent of the TRT except for the longer pyrolysis times (100-500 msec). Fairly large amounts of substance (μg) could be pyrolyzed to a high end-temperature, 1000°C , without noticing any temperature gradient in the sample. When the same amount of sample was placed on a smaller area of the pyrolyzer foil, the amount of products decreased by about 20%.

Introduction:

It is generally considered that pyrolysis should be performed under certain ideal conditions. This means that the pyrolysis temperature shall be constant, the TRT shall be short and the amount of sample shall be small [1,2,3,4].

In an earlier paper [5] cis-1.4-polybutadiene was pyrolyzed at a constant temperature, between 450 and 530°C where the TRT could be regarded as short. It was noticed that under these conditions less than one third of the substance was decomposed, even if the pyrolysis time was increased, leaving an appreciable amount of sample on the platinum foil [5, fig 2].

The aim of this work was to determine the effects resulting from decomposition at temperatures higher than 530°C where pyrolysis conditions are far from ideal. Comparison was made by carrying out similar experiments, but under ideal conditions, i.e. temperatures below 530°C.

In this investigation 96.5% cis-1.4-polybutadiene was pyrolyzed to different end-temperatures, with different TRT and different sample sizes and also the same amount was spread on varying sized foil areas to determine if conditions other than the ideal, could be used when working with qualitative and quantitative practical problems.

Experimental:

Apparatus and working conditions.

The apparatus used has been presented earlier in detail [6]. The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long, 2.6 mm wide. It is heated by two current pulses. The time of the first current pulse can be changed between 3 and 90 msec. This means that the TRT can be changed between 3 and 90 msec too. Actually by choosing a too low first current pulse a longer TRT than 90 msec can be chosen. In this paper TRT:s up to 1 second have been used.

An end-temperature is defined as that temperature which is reached in a known time during which the temperature is increased nearly linearly (see fig 2). The end-temperature does not tell us anything about the temperature at which the sample is pyrolyzed. The end-temperature is not

homogeneous and must be distinguished from the pyrolysis temperature, which can be regarded as constant.

A photodiode is placed under the foil for measuring the temperature of the foil at high values. The photodiode has been temperature calibrated up to 1400°C . For lower temperatures the resistance of the platinum foil was used for temperature measurement [7].

The pyrolyzer is connected to a gas chromatograph so that the products could be extracted directly into the gas chromatograph column. The stationary phase on the column is 15% Apiezon L and the temperature of the column 150°C . The temperature of the pyrolysis chamber is 115°C and the carrier gas flow 20 ml/min. A flame ionisation detector is used. The peak area of the pyrolysis products is measured by an electronic integrator.

Sample preparation.

Different amounts of 96.5% cis-1.4-polybutadiene were dissolved in 2 ml toluene. The viscosity of these solutions varied. This means that when 1 μl of the solution was placed on the platinum foil the area of the sample varied. In the experiments where the sample area was changed, different volumes 0.26; 0.34; 0.50 and 0.95 μl each containing 2.5 μg of sample. The difference in area was about 1 mm^2 to 6 mm^2 . Usually 1 μl from the different sample concentrations was placed on the platinum foil.

Results and discussion:

Pyrolysis to different end-temperatures.

In an earlier paper [5] it was shown that cis-1.4-polybutadiene was not totally pyrolyzed at low temperatures even with long pyrolysis times [5, fig 2]. Figure 1 is a plot of integrator count vs end-temperature from the results of the pyrolysis of 7.4 μg of polybutadiene and the temperature time profile is shown above. It is seen that peak no 1 has a maximum at 1000°C . Peak no 1 consists to the greatest extent of butadiene and the rest of light

hydrocarbons. At temperatures higher than 1000°C it would appear from the shape of peak no 1 that the butadiene concentration decreases and the concentration of light hydrocarbons will increase. At pyrolysis temperatures higher than 1000°C the area of peak no 1 decreases, so does the area of peak no 7 (dimer), and the total amount of pyrolysis products. Peak no 7 reaches its maximum at a lower temperature than 1000°C .

It can be seen from the results that the decomposition products are the same but of different concentration when pyrolyzing at different temperatures and end-temperatures.

Different TRT:s to reach different end-temperatures.

The next experiments show (fig 2) that if the same end-temperatures are reached at different times the results will be nearly the same as those produced when the end-temperatures are reached at the same time (fig 1). It was noticed that after the decomposition at 1400°C , when the end-temperature was reached in 10.5 msec, that the part of the platinum foil containing the substance, was quite black, however. When the time to reach 1400°C was 90 msec the platinum foil was not so black and when the time was 500 msec the platinum foil seemed to be quite clean. In two of the experiments between 1000°C and 1400°C the total amount of products have decreased. In the third experiment the products reached a constant level at about 1000°C . This can depend on the way cis-1.4-polybutadiene decomposes.

It has been seen in this paper and in an other [5] that only one part of the sample, proportional to the temperature, is pyrolyzed. This could depend on differences in the sample weights. Larger molecular weights will initiate the decomposition more easily than smaller. At high temperatures these small molecular weights could be volatilized and have time to escape from the foil before they have been decomposed. This could explain why the amount of products formed was less for a slow TRT.

The black rest on the platinum foil and the decrease in total amounts of decomposition products should be put together. This must indicate that carbonization has taken place.

At temperatures higher than 1000°C it would appear from the shape of peak no 1 that the butadiene concentration decreases and the concentration of light hydrocarbons will increase (as in the experiments in fig 1). This must be due to secondary effects as at least the same amount, or more, of what was formed at a low temperature must be found at a higher temperature reached at a later time.

Different TRT:s used when pyrolyzing at 510°C .

The TRT was changed between 8 msec and about 1 second for experiments in which $7.4\text{ }\mu\text{g}$ samples of polybutadiene were pyrolyzed for different times. The integrator counts from peak no 1 are plotted against time in figure 3. The total amount of monomer formed decreases with increasing TRT and so does the amount of dimer. This cannot be explained by temperature effects. Secondary effects, such as carbonization, probably influence the result.

Different amounts of sample pyrolyzed to 1000°C .

When pyrolyzing different amounts of sample to an end-temperature of 1000°C at a TRT of 8 msec, straight lines were obtained (fig 4) except for the last two points, which were non-linear. The monomer peak area was too small and the dimer peak area too large. This indicates that the temperature within the sample decreases with increasing sample size since the monomer to dimer ratio decreases when the temperature decreases. The temperature in the foil should be homogeneous during the TRT as the cooling effects from the foil fastenings are too slow to produce any effect. It is only the temperature gradient in the sample which should be noticed.

Different areas of the same amount of sample pyrolyzed to 1000°C.

Experiments with 2.5 μg of sample covering different areas were pyrolyzed to an end-temperature of 1000°C reached in 8 msec. The decomposition results are shown in figure 5. The amount of pyrolysis products formed increases with increasing sample area. This could be due to higher temperatures in the sample because the sample is thinner and therefore there is a smaller temperature gradient. However, this explanation would appear to be wrong since the ratio of the integrator counts of peak no 1 and peak no 7 does not decrease with decreasing sample area. The great decrease in the amount of products formed (15%) could not be explained by changes in the temperature. One explanation for the cause of the decrease of the monomer and dimer products when the area of the sample is decreased could be that it is due to that hydrocarbons are converted to carbon.

Different amount of sample pyrolyzed at 445°C.

Similar samples to those pyrolyzed to 1000°C were pyrolyzed at 445°C for 2 seconds. Figure 6 shows the integrator counts of peak no 1 as a function of sample size. The form of the curve in figure 6 cannot be completely explained until further experiments have been done.

1) The viscosity of diluted samples is lower than more concentrated solutions. This means that the diluted sample covers a larger area. 2) There is a temperature gradient in the foil, therefore not all the sample will be pyrolyzed to the same extent. 3) In case of cis-1.4-polybutadiene only a certain amount proportional to the temperature is pyrolyzed. These three things in combination can try to explain the form of the curve.

Different areas of the same amount of sample pyrolyzed at 445°C.

When pyrolyzing at 445°C for 2 seconds, the same weight (2.5 μg) of sample in different volumes, the areas covered by the samples will vary. It is assumed that

small areas should decompose to a larger extent than the larger areas, because the temperature is higher in the middle of the foil, but the temperature gradient in the thicker samples ought to be greater.

In figure 7 the results from the decomposition show that the area of peaks no 1 and 7 increase with increasing pyrolysis area. This could not be explained by the temperature gradient in the sample, when compared with the results in figure 6. Probably these results are caused by secondary effects which seem to occur more frequently when the sample covers a smaller area.

Kinetic studies on the rates of decomposition were carried out on samples covering different areas by pulse pyrolysis [5]. The result was that the reaction half life was longest for the largest area. This seems to support the earlier assumption that the low concentrations will decompose at lower temperatures because of the temperature gradient in the foil and it is the only explanation for the increase in the area of peak no 1 other than less secondary effects.

Conclusions:

When pyrolyzing cis-1.4-polybutadiene for qualitative and quantitative studies end-temperatures up to 1000°C could be used. The temperature should be reached in the shortest possible time and the sample should be placed on a large and constant area of the foil to minimize secondary effects. Large samples should not be used because a temperature gradient may be set up within the sample.

Summarising it is seen that:

- 1) pyrolyzing at non-ideal conditions could be done for qualitative and quantitative studies as long as the end-temperature is not too high and as long as the temperatures are reached in a short time (a few msec).
- 2) samples of a few μg could be used without covering big temperature gradients within the sample.

- 3) secondary effects could probably be reduced if another metal than platinum was chosen in the pyrolyzer.

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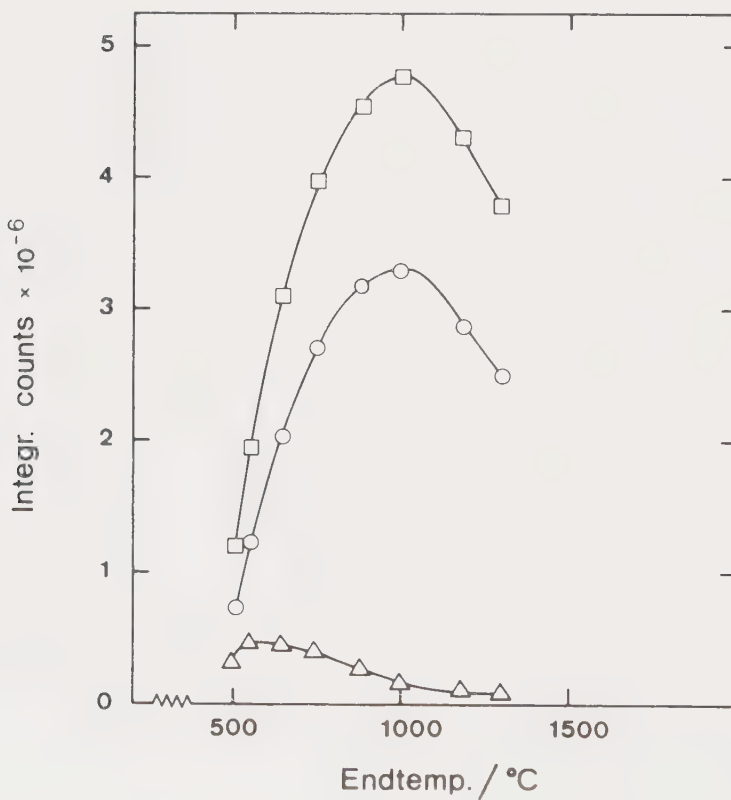
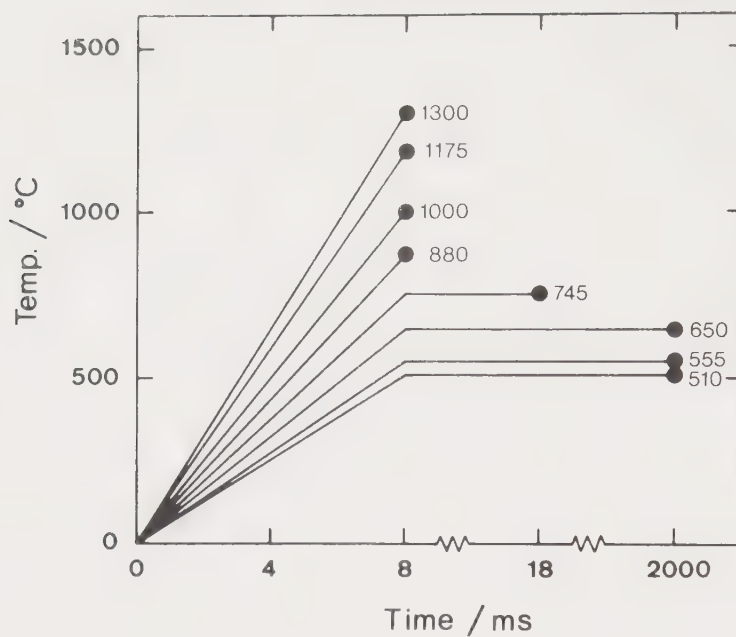


Figure 1: 7.4 µg cis-1,4-polybutadiene pyrolyzed to different end-temperatures reached in the same time. The integrator counts of peak no 1 are plotted against different end-temperatures. The temperature time profile of the different pyrolyses are plotted above.

□ = Σ pyrolysis products

○ = monomer

△ = dimer

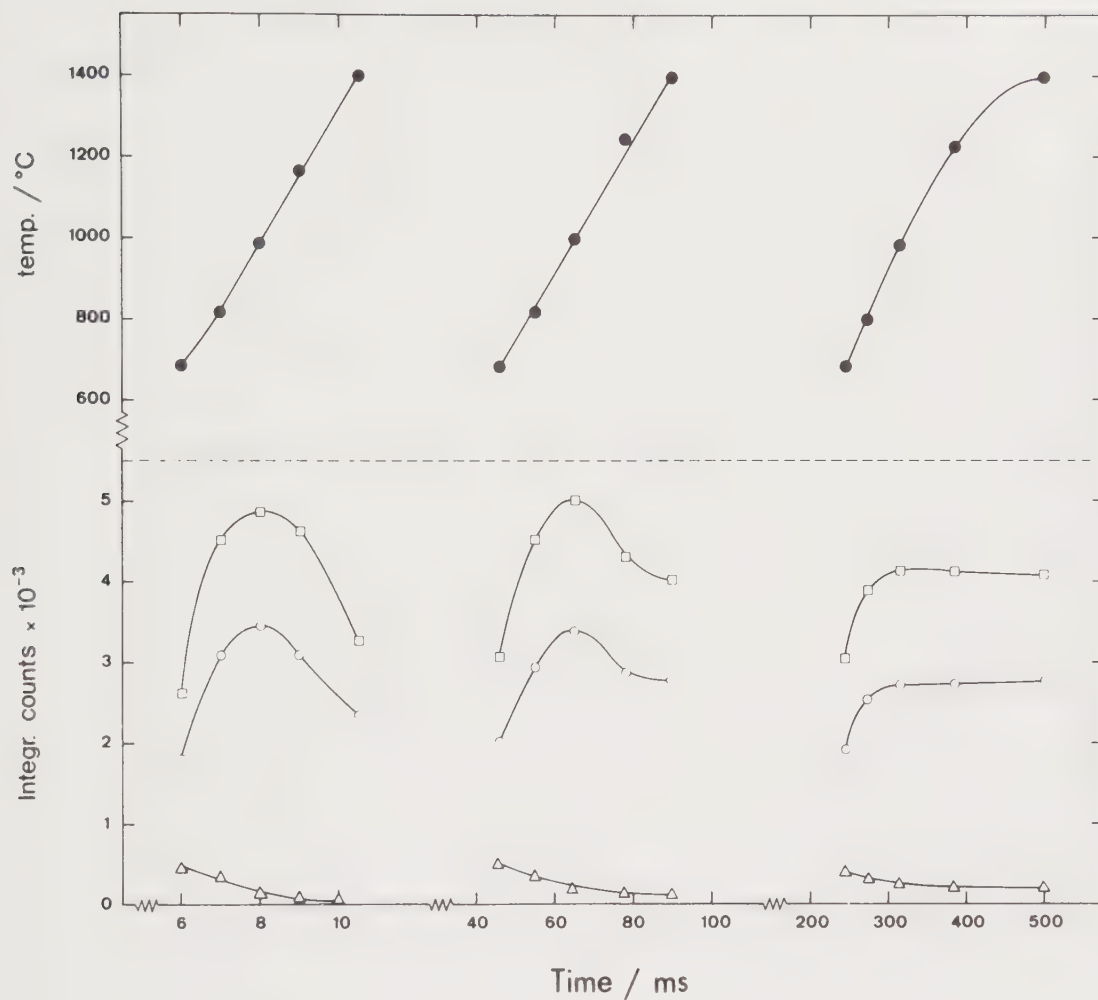


Figure 2: 7.4 μg cis-1.4-polybutadiene pyrolyzed to different end-temperatures reached in different times. The integrator counts from peak no 1 are plotted against the pyrolysis time. The diagrams above show the end-temperatures reached at each time.

$\square$ = Σ pyrolysis products

$\circ$ = monomer

$\triangle$ = dimer

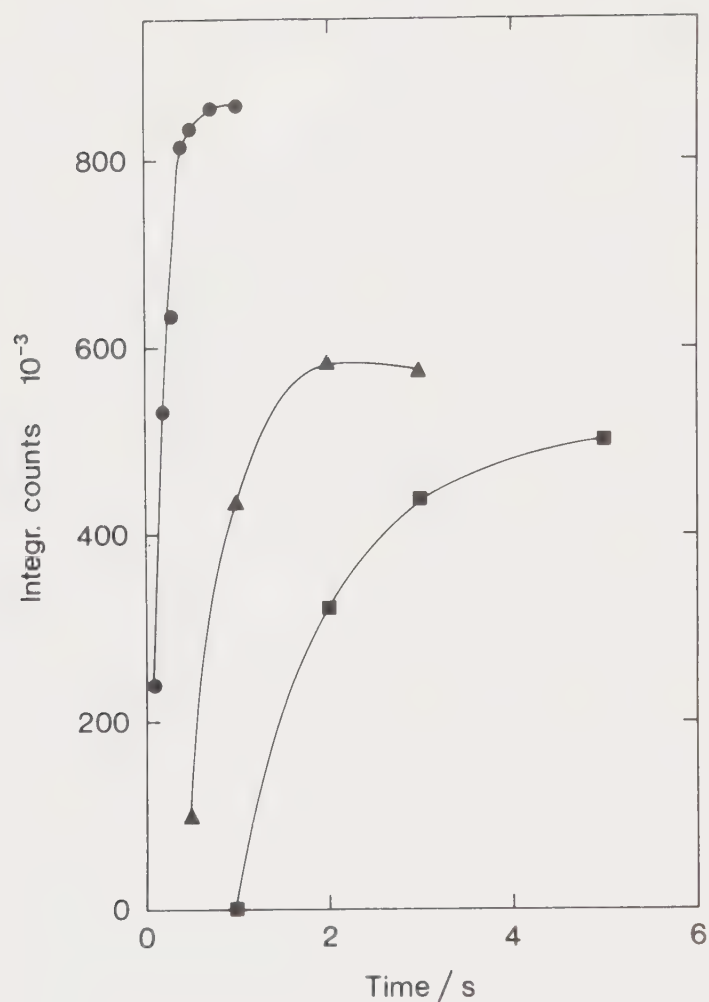


Figure 3: 7.4 μg cis-1,4-polybutadiene pyrolyzed at 510°C and different times. The integrator counts of peak no 1 are plotted against time. Different TRT:s are used for the three curves.

- TRT = 8 ms
- ▲ TRT = 0.5 s
- TRT = 1 s

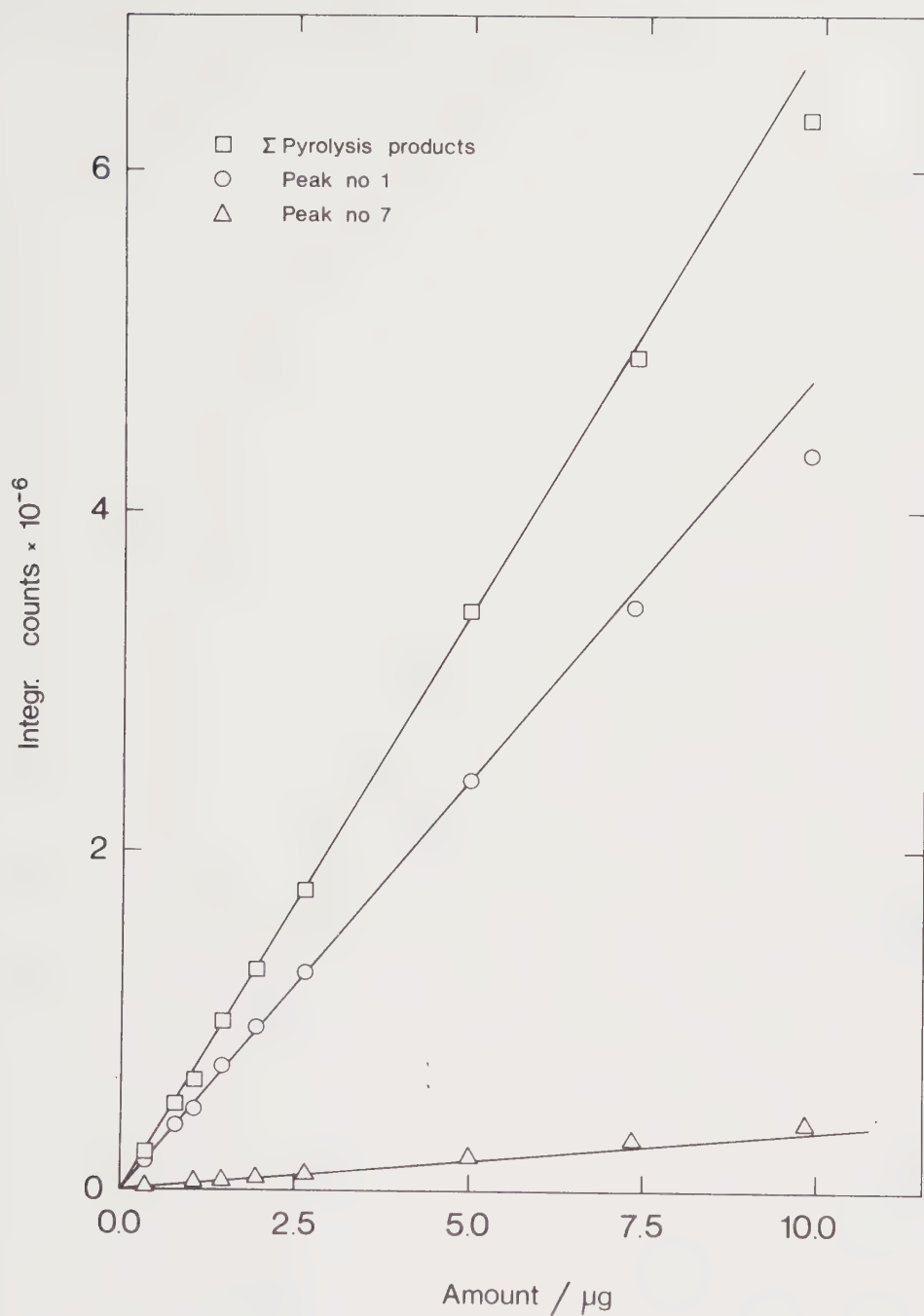


Figure 4: Different amounts of cis-1.4-polybutadiene pyrolyzed to an end-temperature of 1000°C reached in 8 msec. The integrator counts of peak no 1 (monomer), peak no 7 (dimer) and the total amounts of decomposition products are plotted against the amount of polybutadiene.

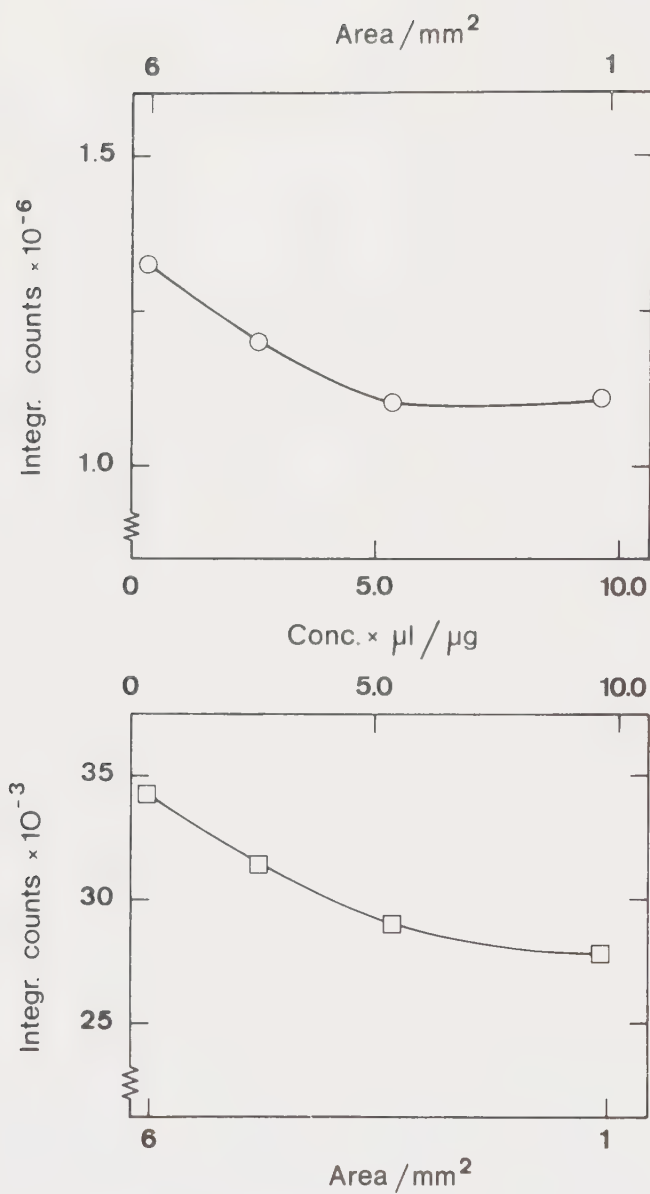


Figure 5: Different areas of 2.5 μg cis-1.4-polybutadiene pyrolyzed to an end-temperature of 1000°C reached in 8 msec. The integrator counts of peak no 1 (monomer) and peak no 7 (dimer) are plotted against the concentrations ($\mu\text{g}/\mu\text{l}$) of the sample and the area of the sample.

○ = monomer

□ = dimer

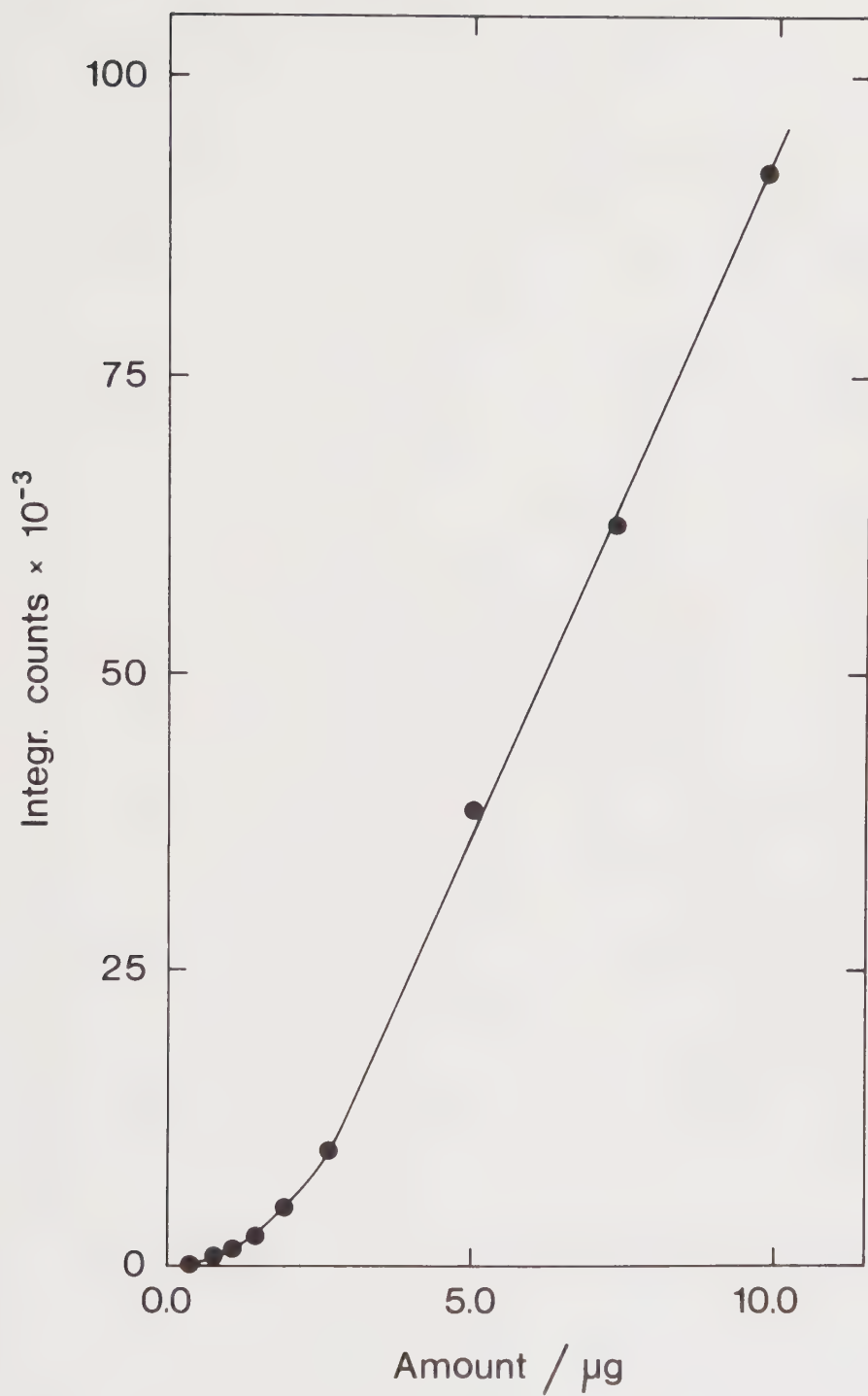


Figure 6: Different amounts of cis-1.4-polybutadiene pyrolyzed at 445°C. The integrator counts of peak no 1 are plotted against the amount of sample.

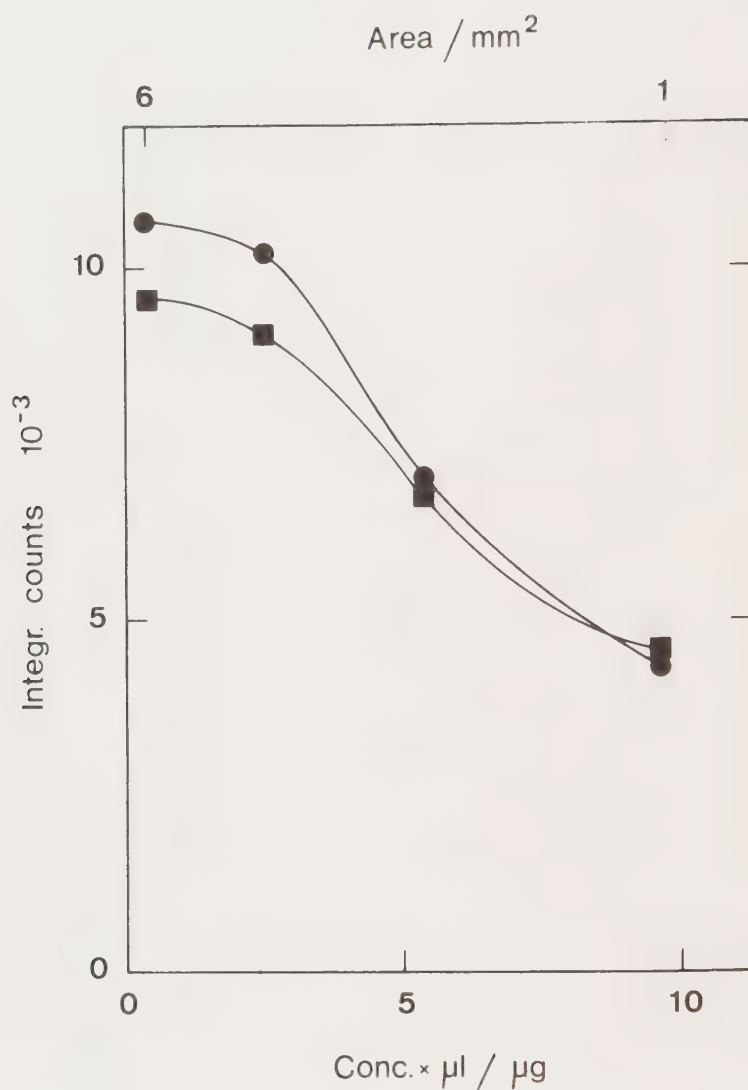


Figure 7: Different areas of 2.5 μg cis-1.4-polybutadiene pyrolyzed at 445°C. The integrator counts of peak no 1 (monomer) and peak no 7 (dimer) are plotted against the concentration (μg/μl) of the sample and the area is valued above.

- = monomer
- = dimer

STUDIES OF PYROLYSIS CONDITIONS FOR QUALITATIVE, QUANTITATIVE AND KINETIC ANALYSES OF POLYSTYRENE BY PYROLYSIS GAS CHROMATOGRAPHY.

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Summary:

Polystyrenes of different molecular weights were decomposed under different pyrolysis conditions. It was shown that the pyrolysis products changed quantitatively but not qualitatively with changing pyrolysis conditions. Different TRT:s did not influence the results except for a parallel displacement of the curves when longer times were used. The best conditions for quantitative analyses were established. It was also shown that quantitative and decomposition studies could be carried out on those products, which constituted only a few per cent of the total decomposition products.

Introduction:

Three different trials [1,2,3] have been carried out to standardize the pyrolysis and gas chromatographic conditions so that comparable pyrograms are obtained independent of the different pyrolysis and gas chromatographic apparatus used. At the third correlation trial, the quality of the pyrograms was very much better than in previous trials, but much more must be done before there is a standardized method [3].

Unlike spectrograms from IR, NMR and MS, the x-axis of

the pyrograms could not be calculated in absolute units. The x-axis is dependent on the gas chromatographic conditions used. This means that it is very difficult to standardize the pyrograms and probably much of the information will be lost.

Even without standardizing the pyrolysis conditions, useful information about decomposition can be collected for different known substances.

For instance if,

- 1) the reproducibility of the pyrolyses,
- 2) identification of decomposition products,
- 3) decomposition to different end-temperatures,
- 4) decomposition at different temperature rise times (TRT),
- 5) decomposition at constant temperatures for different times at an ideal TRT,
- 6) decomposition of different sample sizes, and
- 7) the decomposition on different areas

are examined, valuable information should be obtained, which is quite independent of the gas chromatographic conditions used. It is most important that absolute values be given to the amount of products formed, in other cases where per cent-values have been given most of the information in 1-7 cannot be interpreted. It is also important to present information about the pyrolyzer used because the results could well be dependent on its construction as well as on pyrolysis temperature and pyrolysis time. Some secondary effects that have been reported [4] may be due to these factors. However, secondary effects have not been analysed in this paper.

The aim of this work is to show how the decomposition of different mean molecular weights ($\bar{M}_w$) of polystyrene behave when pyrolyzed under different conditions. Many studies on the decomposition of polystyrene have already been made using differential thermal analysis (DTA) [5], thermal gravimetric analysis (TGA) [6-15] and pyrolysis gas chromatography (PGC) [16-25] but without complete data

on and an understanding of the experimental conditions used little qualitative information can be obtained.

The aim of this work is also to show that the foil pulse pyrolyzer used in this paper and others [4,26-28] could give quantitative information about products, which constitute only a few per cent of the total decomposition products. It will also be shown that kinetic studies can be carried out on these products.

Experimental:

Apparatus.

The apparatus used here has been presented in detail in an earlier paper [26]. The pyrolyzer consists of a thin (0.012 mm) platinum foil, 15 mm long and 2.6 mm wide and is heated by two current pulses. The time of the first pulse is 8 msec and this corresponds to a TRT of 8 msec, provided the amplitude of the first pulse is chosen correctly. The TRT can be lengthened by lowering the amplitude of the first current pulse.

The pyrolysis temperature is measured by the resistance of the foil and by a temperature calibrated photodiode [27]. The pyrolyzer is linked to a gas chromatograph column, which contains a stationary phase of 15% Apiezon L on Chromosorb DMCS 80-100 mesh and the temperature of the column is 175°C. The temperature of the pyrolysis chamber is 115°C and the carrier gas flow 20 ml/min. A flame ionisation detector is used and the peak areas of the pyrolysis products are measured by an electronic integrator.

Sample preparation.

The polystyrene used was anionic polymerized and obtained from Waters Company. Polystyrene of three different average molecular weights was used; $\bar{M}_w$: 2 100, 200 000 and 2 610 000. Different amounts of polystyrene were dissolved in 2 ml of toluene. The viscosity of the same concentrations of the three molecular weights differs, which means

that the areas of the samples differ even when the same volume was placed on the foil.

Results and discussion:

Reproducibility tests.

7.5 μg samples of two different molecular weight species ($\bar{M}_w$ 2 100 and 2 610 000) of polystyrene were pyrolyzed in triplicate at 1015 and 700°C for 8 and 508 msec, respectively, to examine the reproducibility of the pyrolyses. The pyrolyses were carried out over two days. Absolute values from the integrator were used. The reproducibility was good even for small peaks (see table I). The reproducibility of the pyrolysis of polystyrene has been tested on several types of pyrolyzer. Jones found coefficient of variations (S%) between 3% and 6.7% for three different pyrolyzers [20]. Fuchs found for the styrene peak a coefficient of variation of 1.34%, for peak no 1 ($\text{C}_1\text{-C}_5$) 52.2%, the benzene peak 78.5% and for the toluene peak 7.1% [21]. The area of individual peaks were measured as a percentage of the total area of all the peaks and not in absolute values [20,21].

Analyses of the decomposition products.

Qualitative analyses of the pyrolysis products have been made in earlier reports [18,22,23]. The identification of the pyrolysis products was made by comparing the retention values between peaks from known substances and the peaks from the decomposition of polystyrene (see fig 1).

Influence of the pyrolysis temperature.

7.5 μg samples of the three different molecular weight species of polystyrene were pyrolyzed at different temperatures. In figure 2 the integrator counts of styrene formed is plotted against the pyrolysis temperatures and end-temperatures [28]. If pyrolyzing at high enough temperature, the sample will decompose totally, before the end-temperature is reached. In figure 2 these end-temperatures are represented by solid signs. On the other hand if the temperature is low enough and the TRT is

short, compared to the pyrolysis time, the sample will decompose at a constant temperature. In the figure these temperatures are represented by open signs. In the curve obtained from the sample with a $\bar{M}_w$ of 2 610 000 the value at 705°C appears to be in error, but the reproducibility test was made, using the same conditions, on two different days (see table I). The results show a reproducibility of 0.02%. Different $\bar{M}_w$ species give different shaped curves, which could be characteristic and useful for qualitative information.

When comparing the positions of the curves, it can be seen that the curve for $\bar{M}_w$ species of 2 100 lies well below the others. This could be due to low molecular weight species being more easily decomposed to oligomers than high molecular weight species.

The shape of the curves, occurring after the optimum temperature for styrene formation, may probably depend on secondary effects. The peaks for hydrocarbons with lower molecular weights than styrene increase with increasing temperature (see table II, III, IV) and also carbonization of the sample can be observed on the foil. These secondary effects can be compared to the investigation made in [28], where secondary effects, occurring when pyrolyzing polybutadiene, have been determined.

If the results had been presented as a percentage of the total amount of substance formed, much of the information would have been lost (see table II, III, IV). The temperature dependence of styrene formation has been examined earlier, [16-18,24] but absolute values are not given.

Influence of TRT.

When pyrolyzing polystyrene at different TRT:s nearly the same amount of styrene was formed (fig 3), by the end of the pyrolyses. When plotting $-\ln(1 - \frac{C}{C_t})$ against time, the same slope was obtained for the three TRT:s, but the intercept on the x-axis increased, when the TRT was in-

creased (see fig 4). Only one report on the influence of the TRT on decomposition has been found in the literature [28].

Influence of sample sizes.

Different amounts of polystyrene ($\bar{M}_w = 200\ 000$) were pyrolyzed at three different temperatures, one below the optimum for styrene formation, 605°C , one at the optimum, 695°C , and one above the optimum, 900°C .

The calibration curves for styrene (fig 5) show that the influence of sample size was less at 605 and 695°C where the influence of temperature differences was smallest. The integrator counts from the toluene peak from the same experiments were plotted against sample size (fig 6). It is remarkable that a nearly linear response was achieved with a product that accounts for only 2% of the total products formed. The influence of sample size has been shown earlier [30] using another type of pyrolyzer.

Influence of sample areas.

In the same way as the different depths of sample influence the decomposition results (fig 5 and 6) the sample area ought to effect the results. $2.5\ \mu\text{g}$ samples from the three different molecular weight species were pyrolyzed at the optimum temperature for styrene formation and at a temperature below this optimum. Different forms of the curves were expected (see fig 2). It was however shown (fig 7) that the slopes of the curves were very similar. The integrator counts for the styrene peak decreased with decreasing sample area. E.g. for $\bar{M}_w = 2\ 610\ 000$ at 695°C the slope should be positive if the depth of the sample has any influence on the pyrolysis temperature. The only apparent explanation is, that secondary effects increase with decreasing sample area* (compare [28, fig 5 and 7]).

Influence of pyrolysis time at constant temperatures.

$7.5\ \mu\text{g}$ samples of the three different $\bar{M}_w$ species of poly-

* decreasing sample area $\equiv$ increasing sample depth $\equiv$ higher pyrolysis temperature $\equiv$ greater temperature gradient in the sample.

styrene were pulse pyrolyzed [4] for different temperatures (550, 575 and 600°C). The integrator counts for the styrene peak were plotted against time in figure 8 for $\bar{M}_w = 2\,610\,000$. The decomposition-reaction appears to be first-order. $-\ln(1 - \frac{C}{C_t})$ was plotted against time to verify this.

The decomposition of polystyrene has been discussed at length in the literature [5-15, 29]. Two different mechanisms appear to be involved in polystyrene decomposition. The first was thought to be a zero-order reaction and the second a first-order reaction [5,6,8,11]. The high temperature of pyrolysis used in this work did not allow the first mechanism to be examined, but the second reaction mechanism appears to be first-order. Arrhenius plots were made to calculate the activation energy, E_A , for the second reaction mechanism, $E_{A(2)}$, (fig 12) and the overall reaction, $E_{A(\text{overall})}$. k for calculating $E_{A(2)}$ was obtained by measuring the slope of the curves in figures 9, 10 and 11. k for calculating $E_{A(\text{overall})}$ was measured by using the value of 0.69 for $-\ln(1 - \frac{C}{C_t})$, which means that 50% of the styrene was formed (fig 9, 10 and 11). The time corresponding to that value was the reaction half life for the overall formation of styrene. In table V different E_A -values taken from the literature are given together with the methods used and the working temperature interval.

As described above one of the products of polystyrene pyrolysis is toluene and in figure 13 $-\ln(1 - \frac{C}{C_t})$ was plotted against time for the toluene formed when pyrolyzing polystyrene ($\bar{M}_w = 2\,100$). This plot shows that the reaction rate of a decomposition product can be studied even when the amount formed is only a few per cent of the total amount of the decomposition products.

The activation energy for toluene formation is of the same size as that for styrene (fig 13) and the reaction

half life is also the same (table VI). This suggests that toluene is formed from the styrene and should be considered a product of a secondary reaction.

Farré-Rius and Guiochon [31] have calculated the theoretical half-decomposition times for polystyrene. These values do not agree with the values presented in table VI.

Acknowledgements:

The authors wish to thank Dr Terence Steenson for improving the English of the manuscript.

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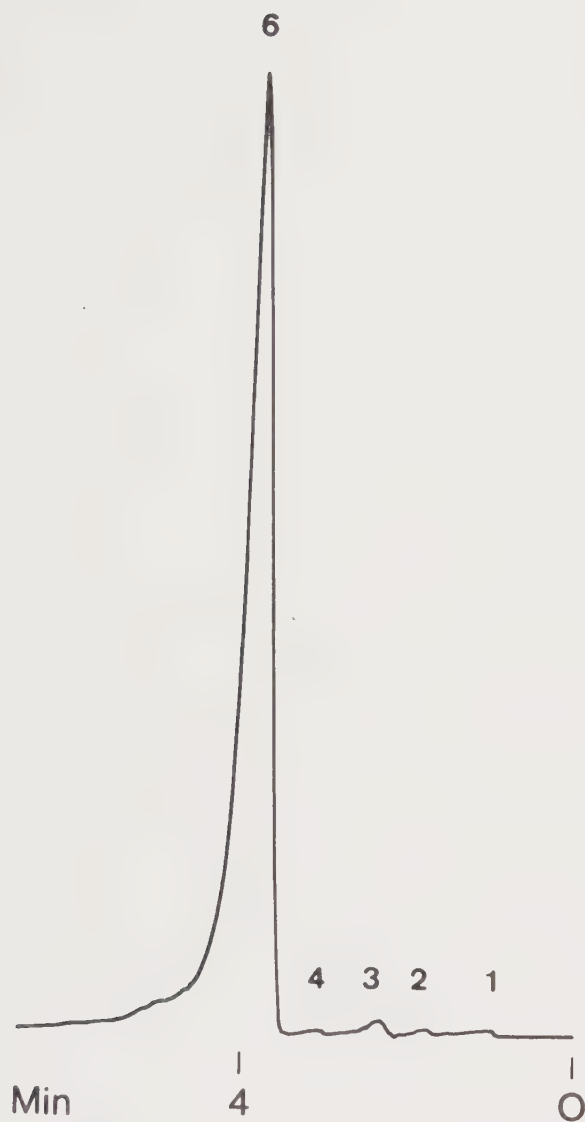


Figure 1: Pyrogram for polystyrene. 7.5 μ g pyrolyzed at 875°C for 8 msec.

- 1) light hydrocarbons (C_1-C_5)
- 2) benzene
- 3) toluene
- 4) ethylbenzene
- 6) styrene

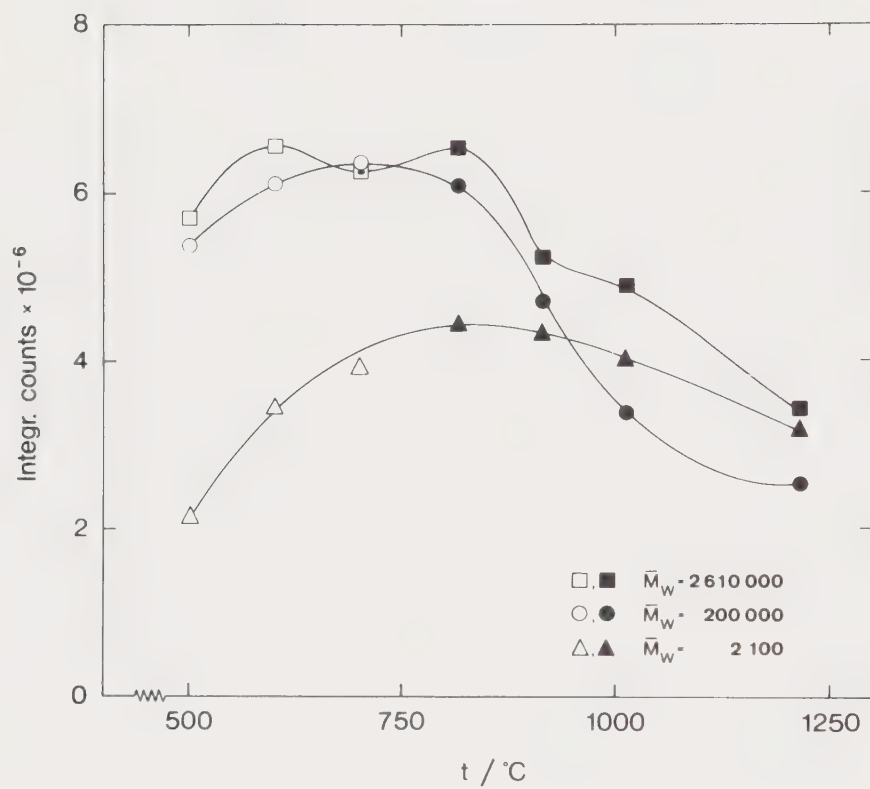


Figure 2: The integrator counts of the styrene peak obtained at different pyrolysis temperatures and end-temperatures.

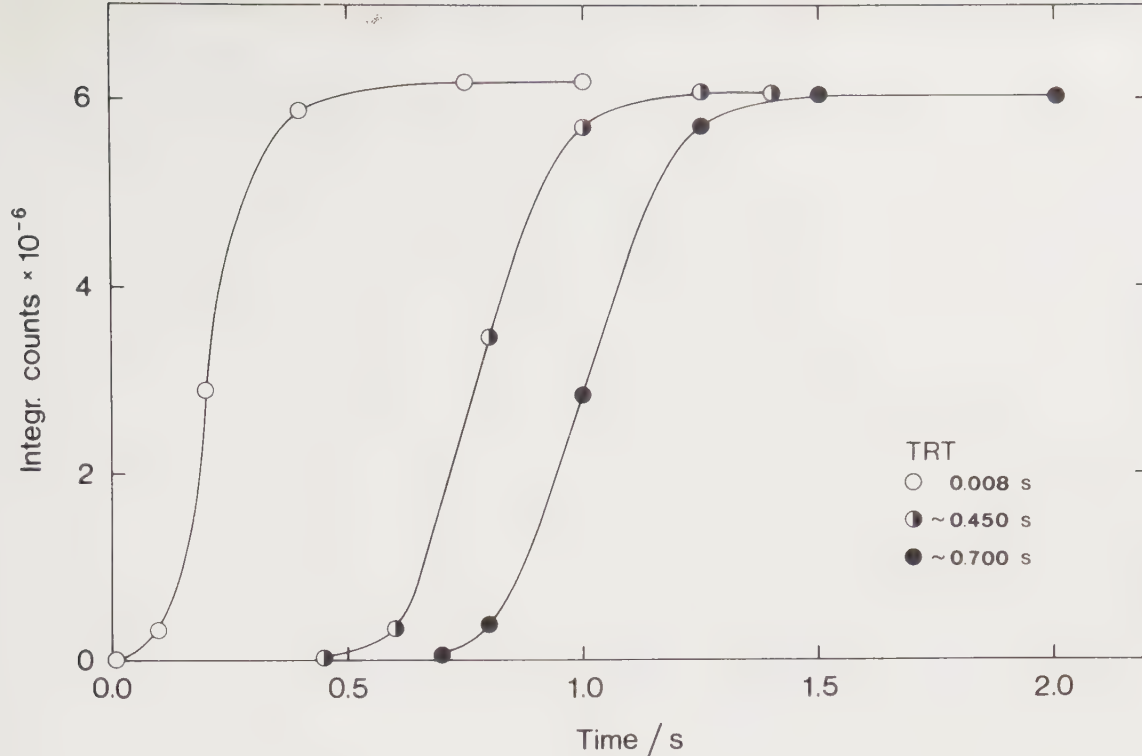


Figure 3: 7.5 μg polystyrene ($\bar{M}_w = 200\,000$) pyrolyzed at 600°C for different times and TRT:s. The integrator counts from the styrene peak plotted against pyrolysis time.

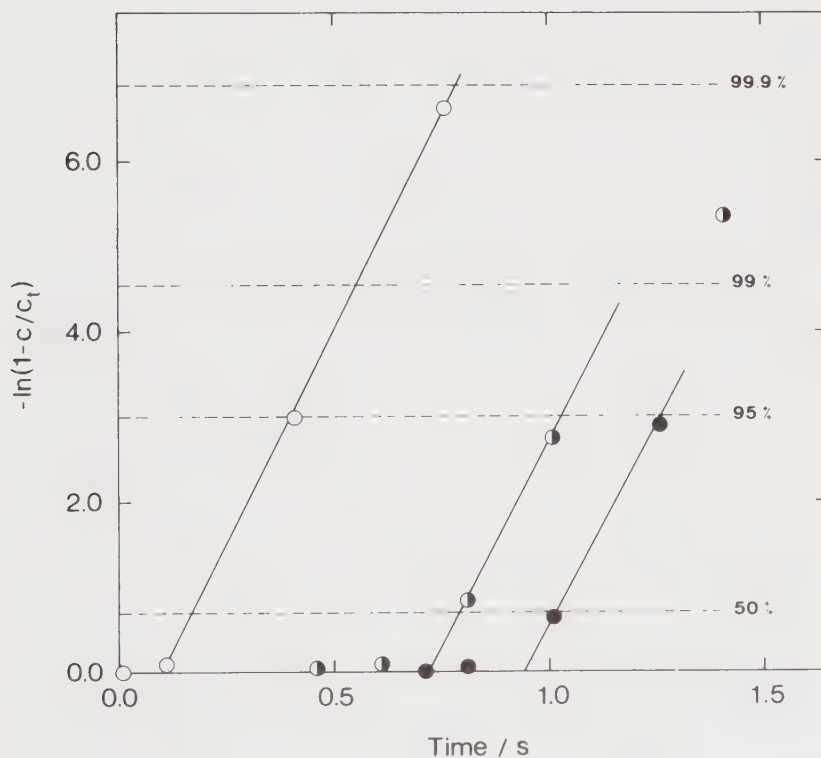


Figure 4: 7.5 μg polystyrene ($\bar{M}_w = 200\,000$) pyrolyzed at 600°C for different times and TRT:s. $-\ln(1 - \frac{C}{C_t})$ plotted against time.

C = integrator counts of the styrene peak formed at each time; C_t = integrator counts of the styrene peak totally formed.

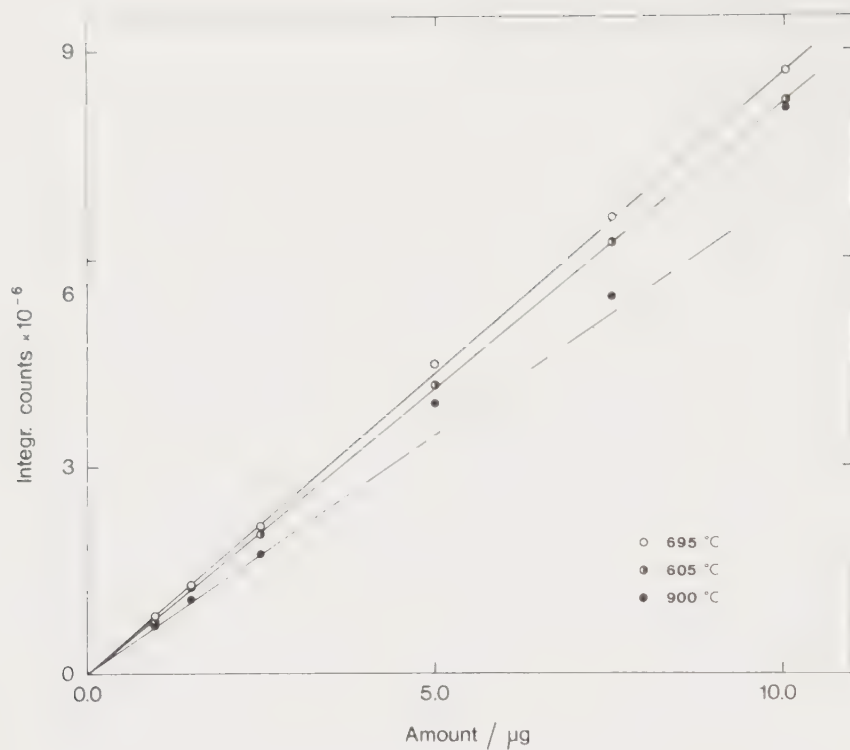


Figure 5: Different amounts of polystyrene ($\bar{M}_w = 200\,000$) pyrolyzed at three different temperatures. The integrator counts from the styrene peak plotted against sample size.

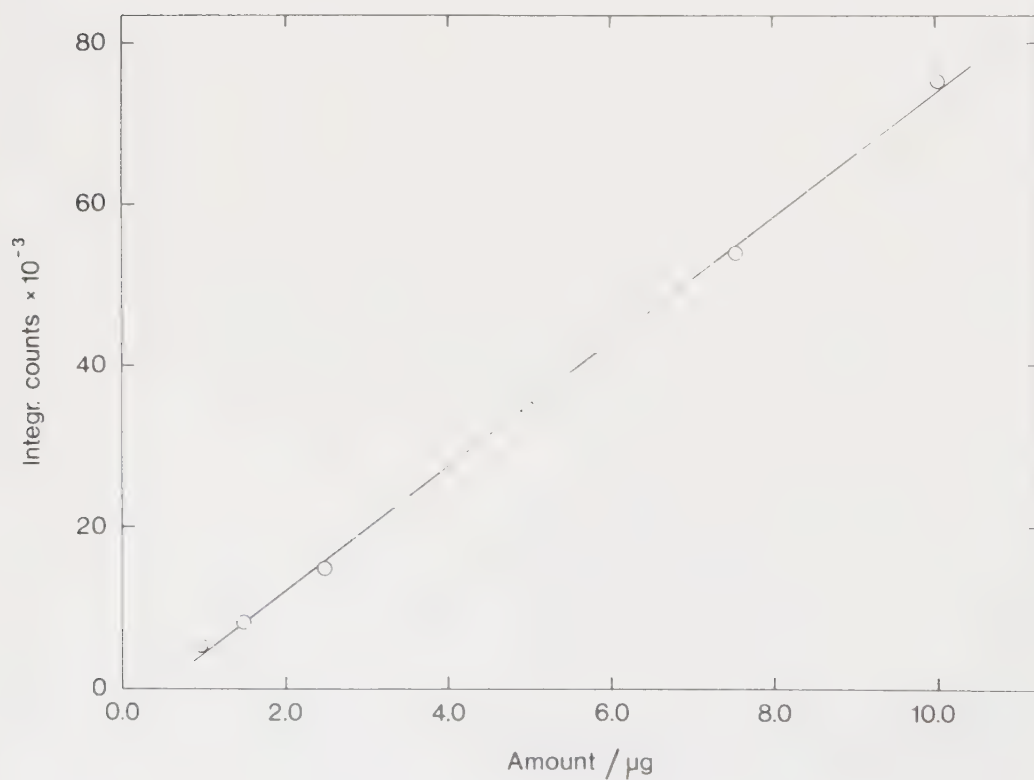


Figure 6: Different amounts of polystyrene ($\bar{M}_w = 200\,000$) pyrolyzed at 695 °C. The integrator counts from the toluene peak plotted against sample size.

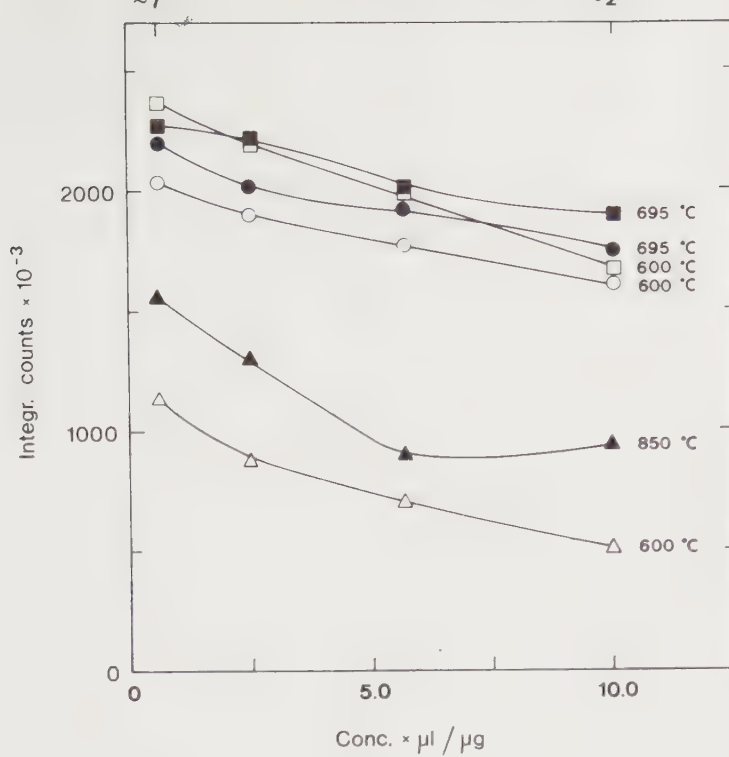


Figure 7: Different areas containing 2.5 μg polystyrene pyrolyzed at two temperatures.

$\square, \blacksquare \bar{M}_w = 2\,610\,000$ where unfilled means
 $\circ, \bullet \bar{M}_w = 200\,000$ the actual pyrolysis
 $\triangle, \blacktriangle \bar{M}_w = 2\,100$ temperature and filled
means end-temperature.

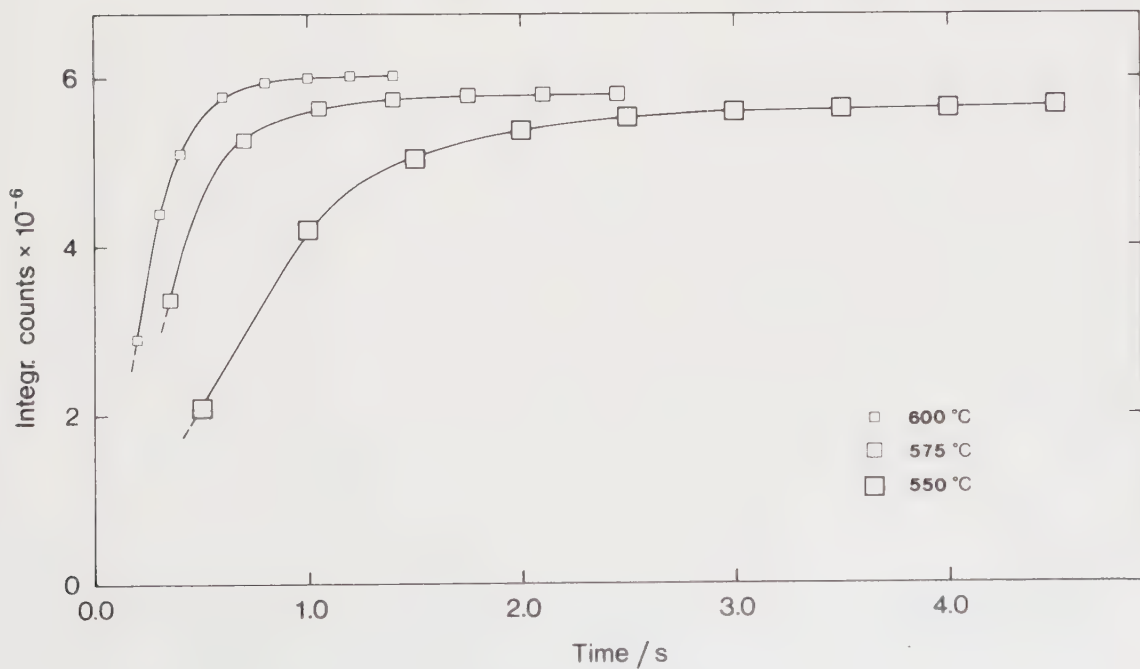


Figure 8: 7.5 μg polystyrene ($\bar{M}_w = 2\,610\,000$) pulse pyrolyzed at different temperatures. The integrator counts from the styrene peak plotted against time.

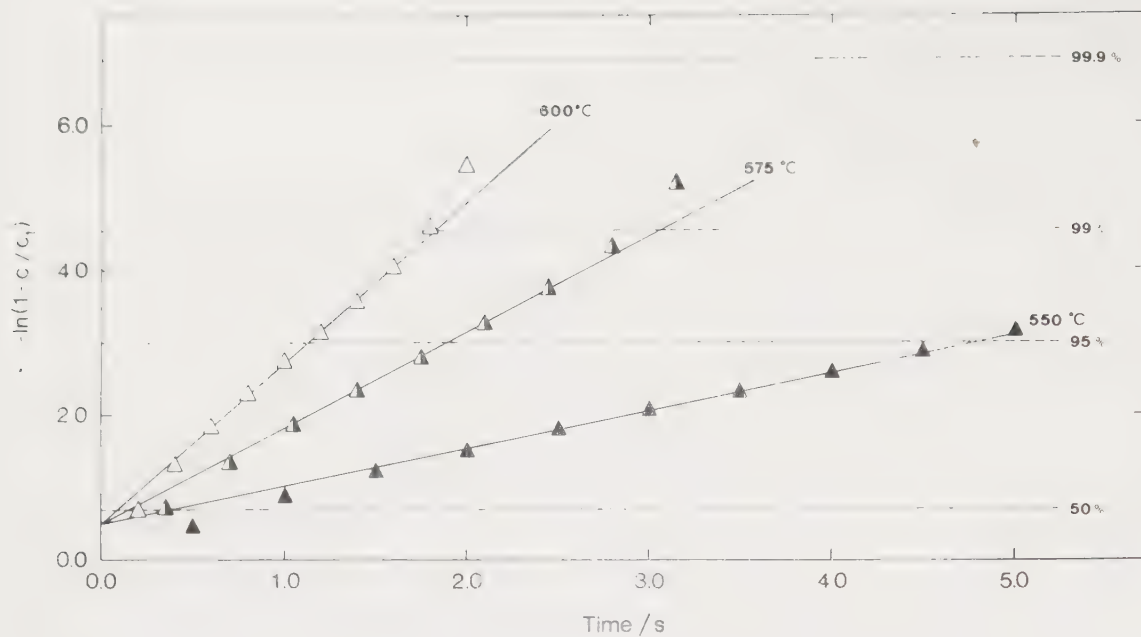


Figure 9: $-\ln(1 - \frac{C}{C_t})$ plotted against time for the formation of styrene when pyrolyzing polystyrene ($\bar{M}_w = 2100$) at different temperatures.

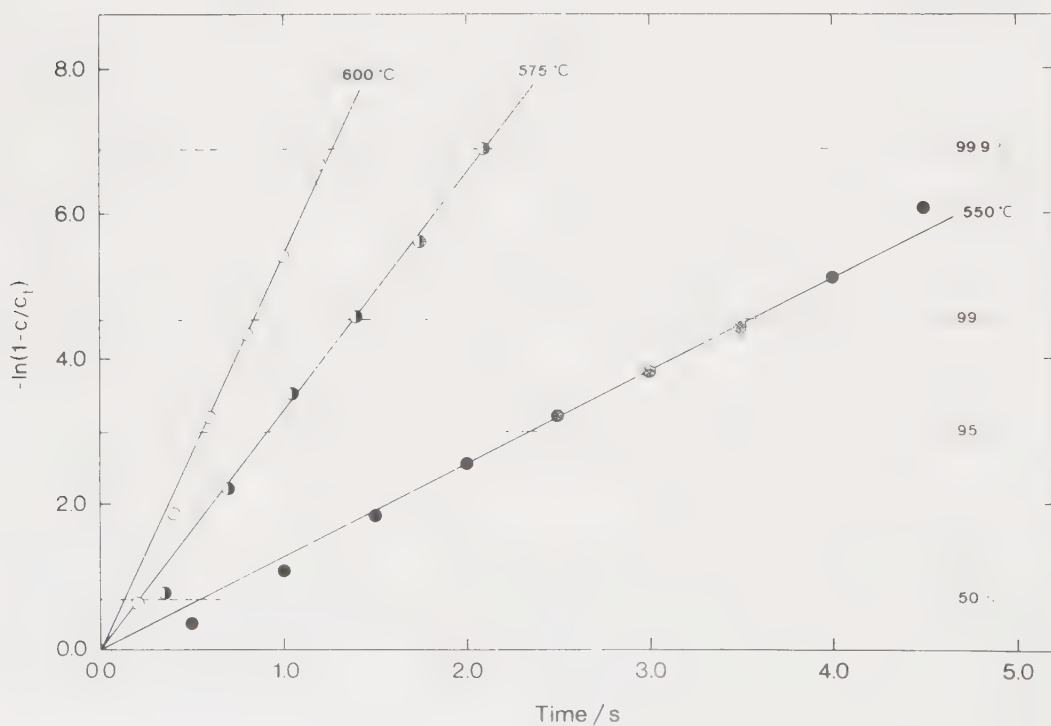


Figure 10: $-\ln(1 - \frac{C}{C_t})$ plotted against time for the formation of styrene when pyrolyzing polystyrene ($\bar{M}_w = 200000$) at different temperatures.

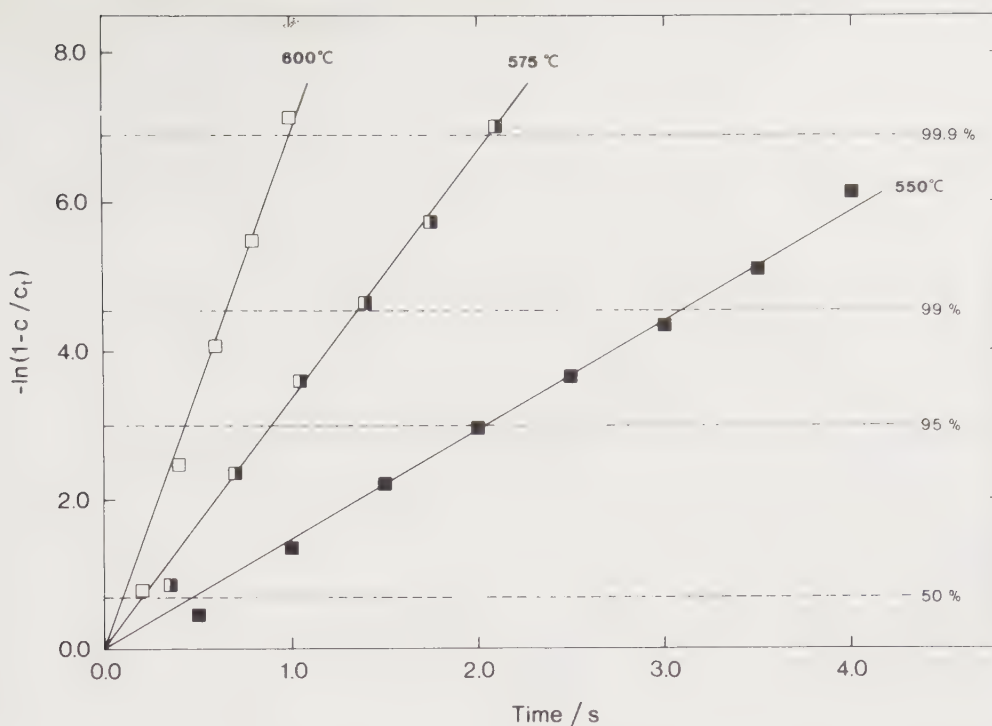


Figure 11: $-\ln(1 - \frac{C}{C_t})$ plotted against time for the formation of styrene when pyrolyzing polystyrene ($\bar{M}_w = 2\,610\,000$) at different temperatures.

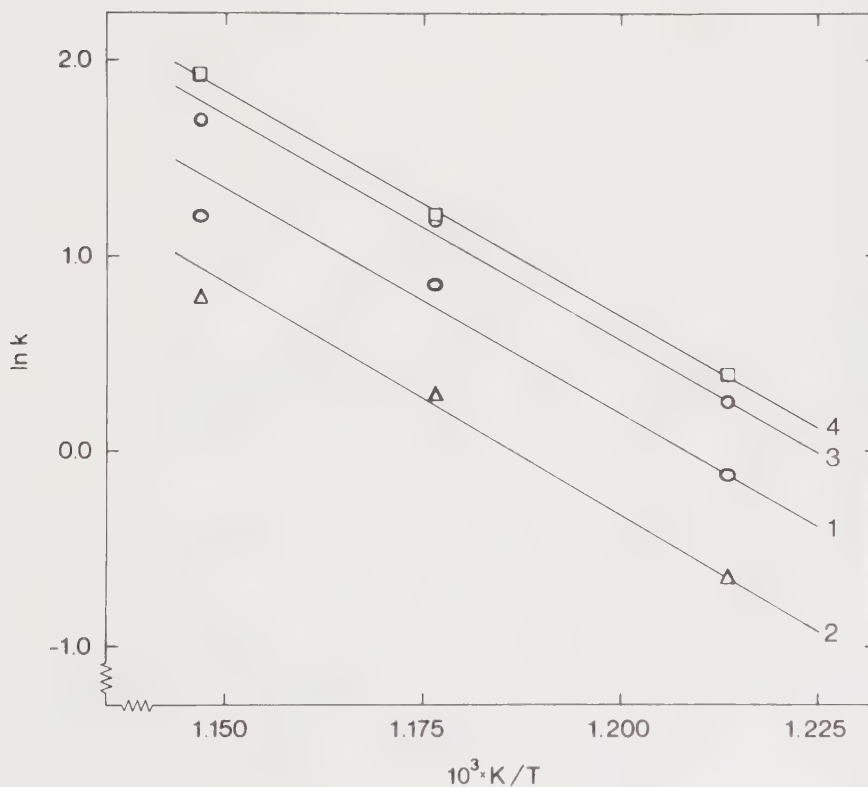


Figure 12: Arrhenius plots for the two decomposition products toluene (curve 1) and styrene (curve 2, 3, 4) formed when different $\bar{M}_w$:s of polystyrene are pyrolyzed. $\bar{M}_w = 2\,100$, curve 1 and 2; $\bar{M}_w = 200\,000$, curve 3; $\bar{M}_w = 2\,610\,000$, curve 4.

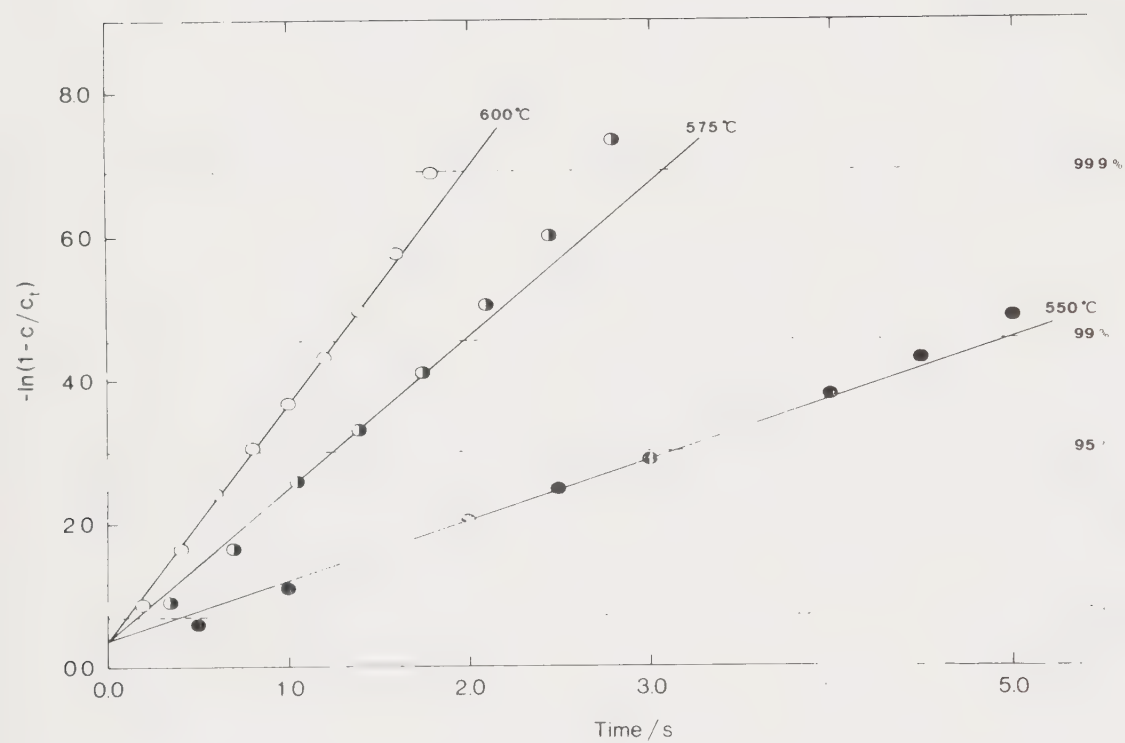


Figure 13: $-\ln(1 - \frac{C}{C_t})$ plotted against time for the formation of toluene when pyrolyzing polystyrene ($\bar{M}_w = 2100$) at different temperatures.

Table I: Reproducibility of polystyrene pyrolysis. Integrator counts for the first seven peaks are tabulated.

Peak no Run date	1	2	3	4	5	6	7
$\bar{M}_w = 2100$ at 1015°C for 8 msec.							
17.2.75	196220	107806	136829	56413	19295	4007428	251881
17.2.75	193318	99301	135704	56804	17908	3965554	253737
18.2.75	197846	110042	139153	57401	19477	4007635	252198

$\bar{x}$	195795	105716	137229	56873	18893	3993539	252605
S/%	1.2	5.4	1.3	0.9	4.5	0.6	0.4
$\bar{M}_w = 2610000$ at 700°C for 508 msec.							
19.2.75	3909	3997	53728	5851		6266930	383178
19.2.75	3819	3849	54879	5669		6264931	414654
20.2.75	4567	4265	53658	5654		6266767	424896

$\bar{x}$	4098	4037	54088	5725		6266209	407576
S/%	10.0	5.2	1.3	1.9		0.02	5.3

Table II: 7.5 μg polystyrene ($\bar{M}_w = 2\ 100$) pyrolyzed at different temperatures. Integrator counts from the different peaks are tabulated.

Temp/ $^{\circ}\text{C}$	Time/s	Peak no	1	2	3	4	5	6	7	8	9	10	Total counts
500	60	counts	15611	795	59779	1690		2126517	45357				2249749
		%	0.7	0.04	2.6	0.08		94.5	2.0				
600	1	counts	40669	2985	85714	7485		3425106		21562			3583521
		%	1.1	0.08	2.4	0.2		95.6		0.6			
700	0.5	counts	64260	5302	84672	12079		3893869	187060	198112			4445354
		%	1.4	0.1	1.9	0.3		87.6	4.2	4.4			
815	0.008	counts	95223	12822	69443	20885		4415735	219122	132659	58177	53671	5077737
		%	1.9	0.2	1.4	0.4		87.0	4.3	2.6	1.1	1.0	
915	0.008	counts	144963	47377	88973	41814		4219202	249860	112818	116537	57058	5078602
		%	2.8	0.9	1.8	0.8		83.1	4.9	2.2	2.3	1.1	
1015	0.008	counts	197846	110042	139153	57401	19477	4007635	252198	127321	102332	34594	5047999
		%	3.9	2.2	2.8	1.1	0.4	79.4	5.0	2.5	2.0	0.7	
1215	0.008	counts	339920	368906	186634	31244	63024	3160290	221345		209025		4580388
		%	7.4	8.0	4.1	0.7	1.4	69.0	4.8		4.6		

Table III: 7.5 μg polystyrene ($\bar{M}_w = 200\,000$) pyrolyzed at different temperatures. Integrator counts from the different peaks are tabulated.

Temp/ $^{\circ}\text{C}$	Time/s	Peak no	1	2	3	4	5	6	7	8	Total counts
500	36	counts	578	1754	57149	1900		5378936	73584		5513901
		%	0.01	0.03	1.0	0.03		97.6	1.3		
600	1	counts	2123	2403	59655	4051		6108531	122285		6299048
		%	0.03	0.04	0.9	0.06		97.0	1.9		
700	0.5	counts	4140	3819	54242	5759		6333958		136905	6538823
		%	0.06	0.06	0.8	0.09		96.9		2.1	
815	0.008	counts	9134	8129	50629	12793		6078660	269127	221294	6649766
		%	0.1	0.1	0.8	0.2		91.4	4.0	3.3	
915	0.008	counts	31488	34211	64531	23648	4562	4706987	295636	180425	5341488
		%	0.6	0.6	1.2	0.4	0.08	88.1	5.5	3.4	
1015	0.008	counts	70639	79027	80008	26560	14406	3380049	219476	178302	4048467
		%	1.7	2.0	2.0	0.6	0.4	83.5	5.4	4.4	
1215	0.008	counts	234014	414112	109369	10830	57482	2514949	157955	153957	3652668
		%	6.4	11.3	3.0	0.3	1.6	68.8	4.3	4.2	

Table IV: 7.5 µg polystyrene ($\bar{M}_w = 2\ 610\ 000$) pyrolyzed at different temperatures. Integrator counts from the different peaks are tabulated.

Temp/°C	Time/s	Peak no	1	2	3	4	5	6	7	8	Total counts
500	28	counts	232	1386	55474	1633		5705737	153738		5918200
		%	0	0.02	0.9	0.03		96.4	2.6		
600	1	counts	1216	2397	58639	3224		6529853			6595329
		%	0.02	0.04	0.9	0.05		99.0			
700	0.5	counts	4567	4265	53658	5653		6266767	424896	109699	6869506
		%	0.07	0.06	0.8	0.08		91.2	6.2	1.6	
815	0.008	counts	9976	11347	51947	18192		6526010	310999	253783	7182254
		%	0.1	0.2	0.7	0.2		90.9	4.3	3.5	
915	0.008	counts	38001	44274	86225	41905		5229217	356337	212543	6008502
		%	0.6	0.7	1.4	0.7		87.0	5.9	3.5	
1015	0.008	counts	117211	140547	137958	47948	20425	4884130	335783	250156	5934158
		%	2.0	2.4	2.3	0.8	0.3	82.3	5.6	4.2	
1215	0.008	counts	373679	681173	183647	19444	76181	3418114	231129	227489	5210856
		%	7.2	13.1	3.5	0.4	1.5	65.6	4.4	4.4	

Table V: Activation energies, E_A , found by different techniques when polystyrene is thermally decomposed.

Author	Method	$\bar{M}_w$	$E_A(1)^{\times}$ mole/kcal	$E_A(2)^{\times}$ mole/kcal	$E_A(\text{overall})^{\times}$ mole/kcal	Working temperature/ $^{\circ}\text{C}$
Reich [5]	DTA	not mentioned	64	74		360-444
Funt, Magill [6]	TGA	4800-2200000	33 $\pm$ 5	50 $\pm$ 5		270-520
Fuoss et al. [7]	TGA	not mentioned			77; 74	400
Andersson, Freemond [8]	TGA	360000	46	60 $\pm$ 5		246-430
Cascaval [9,10]	TGA	300000-700000			50-30	
Kokta et al. [11]	TGA	>360000	33 $\pm$ 5	50 $\pm$ 5	42 $\pm$ 5	250-450
Falb, Berry [12]	TGA	not mentioned	44.5			340-360
Wall [13]	Gravimetry	not mentioned			55	360
Wall et al. [14]	Gravimetry	48500; 5300			51; 45	335-350
Wall et al. [15]	Gravimetry	>24500			49	<353
Cameron, Kerr [29]	Molecular still	255000; 584000	73; 60			280-315
Present work	PGC	2180000	49			280-315
		2610000		46 $\pm$ 3	42 $\pm$ 3	550-600
		200000		46 $\pm$ 3	42 $\pm$ 3	550-600
		2100		47 $\pm$ 3	43 $\pm$ 3	550-600

Table VI: Reaction half lives for the formation of toluene and styrene found when different molecular weights of polystyrene were pyrolyzed at different temperatures.

	M_w 2 100		M_w 200 000	M_w 2 610 000
Pyrolysis temp ^o C	$t_{1/2/s}$ toluene	$t_{1/2/s}$ styrene	$t_{1/2/s}$ styrene	$t_{1/2/s}$ styrene
550	0.60	0.80	0.72	0.64
575	0.27	0.34	0.30	0.23
600	0.16	0.21	0.21	0.18

QUANTITATIVE PYROLYSIS GAS CHROMATOGRAPHY.

Simultaneous determination of two barbituric acids in a tablet formulation.

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Summary:

The amounts of two different barbituric acids, aprobarbital and vinbarbital, in the same tablet were determined by pyrolysis gas chromatography. The acids could easily be separated from four inactive substances in the tablet after conversion to the corresponding sodium salts. The reproducibility of the analyses was better than $\pm 3\%$ for each of the acids.

Introduction:

Barbituric acids have a wide-spread use in pharmaceutical preparations. The quality control usually includes identification and quantitative determination of the active substances and since several barbituric acids may constitute a preparation, an additional separation step becomes necessary. The currently used methods involve ordinary gas liquid chromatography (GLC) [1,2], liquid-liquid chromatography (LLC) [3] or thin layer chromatography (TLC) [4] techniques both for the separation and the quantitation step.

Qualitative analyses of barbituric acids have been made by pyrolysis gas chromatography (PGC) [5-8] but no quantitative analyses have been reported. This may be due to

the poor reproducibility of the analyses which is inturn due to difficulties in achieving reproducible pyrolysis conditions. This paper describes an analytical method using pyrolysis gas chromatography in which much more reproducible pyrolysis conditions are achieved allowing the quantitative determination of barbituric acids.

The investigation has been made on a commercial preparation¹ containing both aprobarbital (A) and vinbarbital (B) (see fig 1). The tablet specification is 50 mg of A and 100 mg of B. The actual amounts in the tablets must not deviate by more than $\pm 10\%$ from the specification.

Experimental:

Apparatus and working conditions.

The apparatus used has been described in detail earlier [9]. Experiments to achieve gas chromatographic conditions that would allow complete resolution of the pyrolysis products were not attempted. The gas chromatographic conditions were similar to those used for the pyrolysis of cis-1,4-polybutadiene [9]. These experiments were carried out to demonstrate that pyrolysis gas chromatography could be applied to analytical problems of the kind in which simplicity, speed and reproducibility are required. The chromatographic peak areas were measured by an electronic integrator.

The residue from the decomposition products of the salts left on the platinum foil were removed by cleaning with water and dilute HCl, followed by heating in a Bunsen flame; if this procedure was not rigidly adhered to the reproducibility was poor.

Sample preparation.

Calibration solutions of aprobarbital (A) were prepared by dissolving 3.6 to 4.8 mg of the substance in 2 ml 0.041M NaOH. Each solution also contained a constant amount of vinbarbital (B), 8.0 mg.

¹Diminal Duplex[®], Astra, Södertälje, Sweden.

Calibration solutions of vinbarbital were prepared by dissolving 7.2 to 9.6 mg in 2 ml 0.041 M NaOH. Each solution also contained 4.0 mg A.

Simulated tablet compositions were obtained by mixing the four inactive substances gelatine, cellulose, magnesium stearate and potatoe starch in the same proportions as in the commercial tablets. Six different tablets were prepared. The amount of the two active substances were varied within the acceptance limits for commercial tablets. The tablet compositions as well as the commercial tablets were dissolved in 25 ml 0.041 M NaOH. The four inactive substances did not dissolve completely and were filtered off. 1 μ l of the filtered solutions was placed on the platinum foil. The solvent, H₂O, was evaporated by an infrared lamp before the pyrolysis.

Results and discussion:

Specific peaks.

In order to make quantitative determinations by pyrolysis gas chromatography, specific decomposition products from each substance must be found.

Figure 2 shows pyrograms of the sodium salts of 2.0 μ g aprobarbital (A), 4.0 μ g vinbarbital (B) and 2.0 μ g A + 4.0 μ g B. The pyrolysis temperature was 550°C and the pyrolysis time 2 seconds. From the pyrograms it can be concluded that peak no 8 is specific for substance A. Peak no 9 is specific for B but probably this peak is too small for quantitative determinations. Peak no 10 seems to be more suitable for quantitative purposes even if it is not specific. In this special case, where A and B are both active ingredients in the pharmaceutical preparation it is possible, by suitable calibration, to correct for the presence in peak no 10, of product from A. This will then allow a quantitative estimation of B to be made.

Reproducibility.

The reproducibility of the pyrolyses was tested at 600°C and the results are shown in table I. The reproducibility of the two peaks, no 8 and no 10, was good, 1.9 and 2.2%, respectively. When using gas chromatography without a pyrolysis unit, standard deviations of the same magnitude are obtained.

However, the error due to sample injection, when carrying out normal GLC, can be decreased when a pyrolysis unit is combined to the chromatograph. The sum of the errors due to both the pyrolysis and GLC may be even less than that found with GLC alone.

Influence of NaOH excess.

In order to investigate the influence of different excesses of NaOH on the decomposition constant amounts of A and B, respectively, were dissolved in different concentrations of NaOH and were pyrolyzed at 550°C for 2 seconds. The results are given in table II.

It is obvious that the integrator counts of peak no 8 decrease with increasing excess of NaOH and the same thing is valid for peak no 10.

Influence of pyrolysis temperature and time.

2.0 µg A and 4.0 µg B were pyrolyzed at different temperatures (table III). The integrator counts of peak no 8 increase with the temperature up to 550°C. On the other hand the integrator counts of peak no 10 have a maximum at 500°C. The influence of the temperature on the decomposition of A is greater than on B.

The time dependence of the decomposition was investigated at 550°C (table IV). It is probable that the decomposition is already finished after 0.2 seconds.

Suitable pyrolysis conditions.

From the information in figure 2 and tables II, III and IV the conditions for the quantitative determination of the two barbituric acids incorporated, as the active ingredients in a commercial tablet preparation, were chosen. The pyrolysis should be performed at 550°C for 2 seconds and the NaOH to acid mole ratio should be kept constant and as close to 1.5 as possible.

At these chosen pyrolysis conditions calibration curves for the two substances A and B were made (fig 3 and 4).

Recovery test.

The solutions from the six simulated tablets were pyrolyzed with varying time intervals between each duplicate. From table V it can be seen that there is complete reproducibility even when a repeat pyrolysis of a duplicate sample is made after a long time interval when other pyrolyses have been made. The calibration curves were used (fig 3 and 4) and the recoveries of A and B were calculated (table V). The recovery of A is too high. Reasons for this may be found among the errors discussed below. The reproducibility is better than $\pm 2\%$ for all tablets except for tablet V and this result could well be due to experimental error.

Errors.

The excess of NaOH is critical for the results. If a tablet contains high concentrations of active substances the excess of NaOH will be less than the excess used in obtaining the calibration curves. This means that the integrator counts give more numerous decomposition products (table II) and the calculated values will be too high. Conversely, if there are small amounts of active substance the excess of NaOH will be high and the values calculated from the calibration curves will be too low.

Peak resolution will influence the results. From figure

2 it can be seen that peak no 9 interferes with both peak no 8 and peak no 10.

If there is more or less of A in the sample than in the calibration curve for B, the addition proportion due to A in peak no 10 will vary. This means that the calculated amount of B found will either be too high or too low.

As mentioned above the cleaning of the platinum foil is important for the reproducibility of the temperature and the effective area of the foil.

Conclusions:

Pyrolysis gas chromatography is an acceptable quantitative method if different parameters are kept constant, e.g. excess of NaOH, pyrolysis temperature and time.

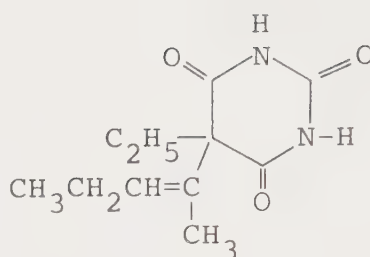
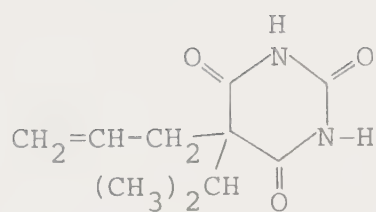
In this case the reproducibility of peaks which gave less than one per cent of the total products, was between 2 and 5 per cent. This means that age effects in the tablets could probably be detected because changes of small peaks can be registrated. By identifying the peaks from the decomposition the aging process would be understood.

Acknowledgements:

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A

Aprobarbital

5-allyl-5-isopropyl

M = 210

B

Vinbarbital

5-ethyl-5-(1-methyl-1-butenyl)

M = 224

Figure 1

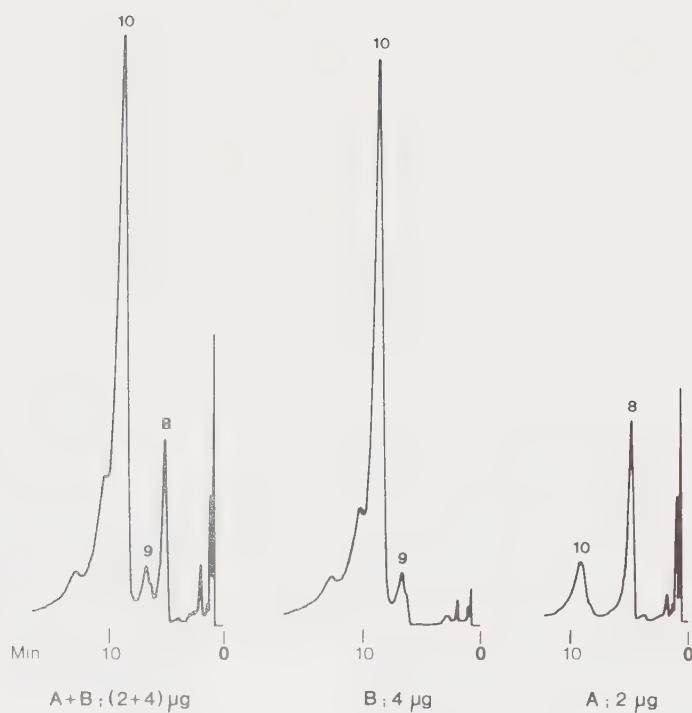


Figure 2: 2 µg of aprobarbital (A), 4 µg of vinbarbital (B) and (2+4) µg A+B were pyrolyzed at 550°C for 2 seconds.

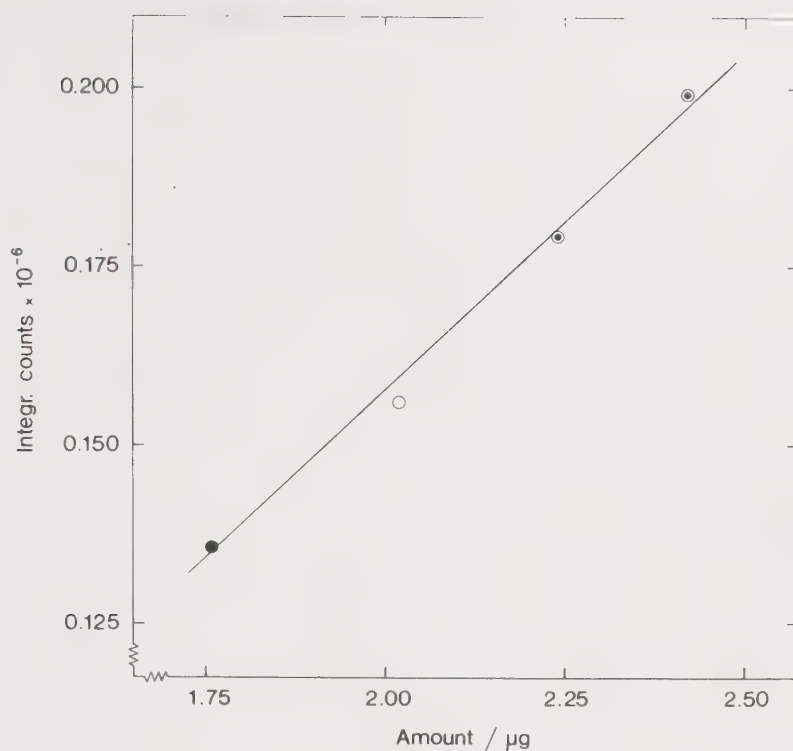


Figure 3: Calibration curve for peak no 8. Different amounts of aprobarbital with a constant amount of vinbarbital, 4.0 μg , were pyrolyzed at 550°C. ○ single value; ◐ mean of two values; ● mean of five values.

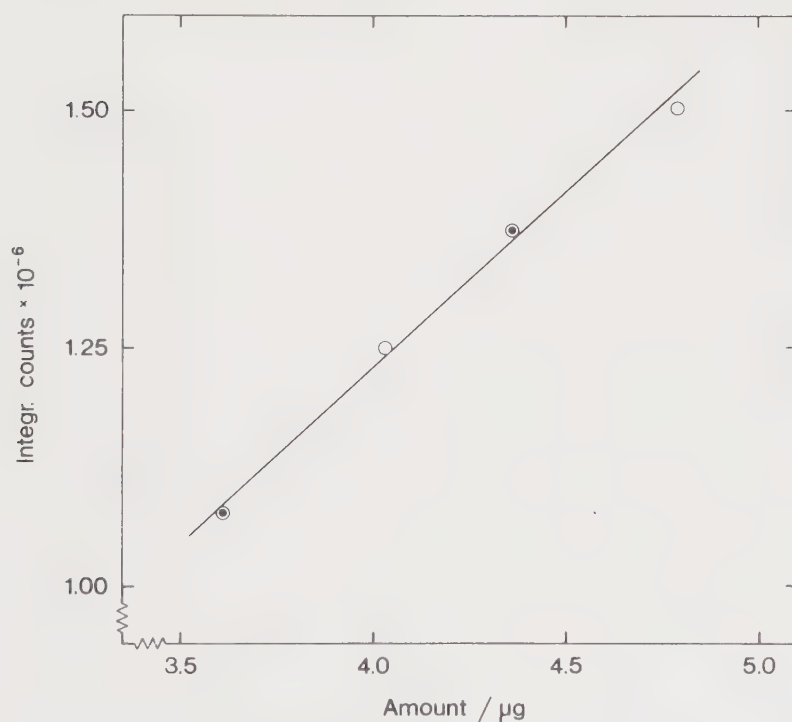


Figure 4: Calibration curve for peak no 10. Different amounts of vinbarbital with a constant amount of aprobarbital, 2.0 μg , pyrolyzed at 550°C for 2 seconds. ○ single value; ◐ mean of two values.

Table I: About 2 µg aprobarbital and 4 µg vinbarbital from a commercial tablet were pyrolyzed five times at 600°C for 2 seconds. Integrator counts from the different peaks and the total amount of pyrolysis products, Σ , are tabulated.

Peak no	1	2	3	4	5	6	7	8	9	10	Σ
Pyrolysis no											
1	68738	22760	17023	36820	8911	10855	10870	162522	120588	1199587	1658674
2	67471	22356	16880	37140	8769	10985	11537	160461	126966	1220609	1683174
3	68294	23286	16746	37228	8257	10492	10423	166651	120667	1257638	1719682
4	70305	23576	16916	36765	8613	10229	10229	168404	113115	1245576	1703728
5	72488	24332	17522	39636	9308	10870	10910	168250	114798	1241879	1709693
S	1982	761	299	1201	386	316	507	3581	5495	22989	24294
$\bar{x}$	69459	23262	17017	37517	8771	10686	10794	165257	119227	1233058	1694990
S%	2.9	3.3	1.8	3.2	4.4	3.0	4.7	2.2	4.6	1.9	1.4

Table II: 2.0 μg aprobarbital (A) and 4.0 μg vinbarbital (B) pyrolyzed at 550°C for 2 sec. The excess of NaOH was varied. Integrator counts from peaks no 8, 9, 10 and the total amount of pyrolysis products, Σ , are tabulated.

Peak no Mole ratio	8	9	10	Σ
A=2.0 μg				
1.05	167878		80462	315635
1.25	159009		72663	302097
1.50	157313		66471	295706
2.00	142808		42209	281691
4.00	82482		21901	211217
B=4.0 μg				
1.05		64108	1128605	1208143
1.25		73215	1110498	1200183
1.50		78306	1082936	1184329
2.00		89815	1053020	1180510
4.00		127496	705408	929845

Table III: 2.0 μg aprobarbital (A) and 4.0 μg vinbarbital (B) pyrolyzed for 2 sec at different temperatures. Integrator counts for the three peaks no 8, 9, 10 and the total amount of pyrolysis products, Σ , are tabulated.

Peak no Temp $^{\circ}\text{C}$	8	9	10	Σ
A=2.0 μg				
450	89406		44111	176555
500	112668		38621	214283
550	157313		66471	295706
600	155128		60461	323843
B=4.0 μg				
450	287	65110	1062580	1137480
500	312	74890	1102239	1193991
550	272	78306	1082936	1184329
600	2408	96682	1037512	1206630

Table IV: 2.0 μg aprobarbital (A) and 4.0 μg vinbarbital (B) pyrolyzed at 550°C at different times. Integrator counts for the three peaks no 8, 9, 10 and the total amount of pyrolysis products, Σ , are tabulated.

Peak no Time sec	8	9	10	Σ
A=2.0 μg				
0.05	129277		39457	193408
0.2	189774		95521	347771
2.0	180567		101682	373149
B=4.0 μg				
0.05		48265	1090720	1144808
0.2		75234	1193444	1281516
2.0		75575	1205709	1301512

Table V: Recovery test of simulated and commercial tablets.

Pyrolysis no	Simulated tablet	A mg	B mg	Found A mg	Found B mg	Recovery A%	Recovery B%
27	I	50.22	110.0	50.50	107.8	100.7	97.6
13	"			50.62	107.0		
4	II	45.18	108.5	47.88	107.0	105.0	97.9
14	"			47.00	105.5		
7	III	54.93	90.5	57.00	94.0	104.9	104.0
17	"			58.25	94.2		
8	IV	50.36	100.8	52.38	99.8	105.5	99.0
18	"			53.88	99.8		
9	V	55.12	109.9	54.25	107.0	101.4	99.7
19	"			57.50	112.2		
10	VI	45.14	90.1	45.00	84.0	100.6	94.9
20	"			45.88	87.0		
Commercial tablet				Found A mg	Found B mg	Expected value A mg	Expected value B mg
28	I			50.5	101.9	50 $\pm$ 5	100 $\pm$ 10
29	II			50.9	102.6	50 $\pm$ 5	100 $\pm$ 10

Tryckbaren
Lund 1975